A CLASS-BOOK OF ORGANIC CHEMISTRY

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VOL. I.

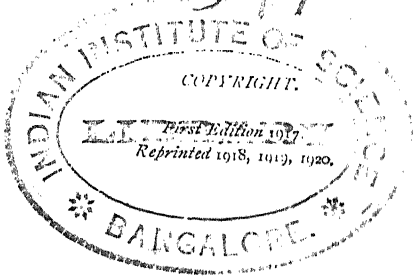
FOR FIRST YEAR MEDICAL STUDENTS
AND
SENIOR SCIENCE STUDENTS IN SCHOOLS

MACMILLAN AND CO., LIMITED
ST. MARTIN'S STREET, LONDON

1920

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First Edition 1917
Reprinted 1918, 1919, 1920.

PREFACE

THIS little volume has been written as an introduction to organic chemistry for the use of first year medical students and for senior science students in schools. By treating the theoretical and practical sides of the subject concurrently, it is intended that the book may serve the double purpose of text-book and laboratory manual. It is divided into three parts. In the first part the general principles underlying determinations of purity, empiric and molecular formulæ and structure, are explained and illustrated by a careful study of two of the most familiar and most easily procurable organic substances, viz., methyl and ethyl alcohols. In the second part, the aliphatic compounds are described in a more systematic fashion; and the third part is devoted to a brief account of the more important members of the aromatic series. It is hoped that the book will fill a gap and serve the purpose for which it was written.

I wish to acknowledge the valuable help I have received from Mr. A. T. Simmons in the correction of the proofs.

J. B. COHEN

THE UNIVERSITY, LEEDS.
April, 1917.

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INTRODUCTION

ORGANIC chemistry, until about the middle of the nineteenth century, included only materials derived from the products of animal and plant life. The name *organic* was used to denote the source of these products from organised matter, and at the same time it served to distinguish them from the mineral or inorganic materials of the inanimate world.

This original meaning of the term organic has long since disappeared. Whilst a little more than half a century ago organic compounds derived from animal and vegetable sources, such as sugar, starch, oils, fats, gums, resins, etc., could be counted only by hundreds, the number to-day exceeds one hundred thousand, and they are mainly artificial products of the laboratory and the chemical works.

We shall learn in the sequel the reason of this sudden growth of organic chemistry in recent years, and the change in the nature of its materials. In passing, it may be briefly stated to be due to the blending of science and industry. Thus the art of the dyer has been revolutionised by the introduction of artificial dye-stuffs; the skill of the surgeon has been greatly assisted by the discovery of anæsthetics and antiseptics; the photographer has to thank organic chemistry for his "developers"; artificial drugs of established purity are used in medicine, artificial essences in perfumery. Moreover, the organic chemist

has the task of controlling such industries as tanning, the manufacture of sugar, soap, inks, paper, glue and gelatine, rubber, artificial silk, explosives, &c. But in addition to the application of science to industry there were other causes at work which awakened organic chemistry from its long torpor.

It must be remembered, in the first place, that inorganic substances—that is to say, the principal derivatives of the metals and non-metals—were divisible into three main classes, namely, **bases** and **acids** and their combinations, which gave rise to **salts**. Moreover, each base, acid, and salt consisted of certain elements which characterised the substance. Hydrochloric acid was composed of hydrogen and chlorine, and no other compound of these two elements was known. Caustic soda consisted of sodium, hydrogen, and oxygen, and it was the only existing substance which contained these three elements. Similarly, the salt formed by the union of these two compounds, namely, sodium chloride, or common salt, was the only known salt containing sodium and chlorine.

Each combination of elements usually represented one substance. There were some few exceptions, such as the different oxides of lead, but their properties did not greatly differ and their relationships were easily explained. But it was found that the compounds derived from living matter always contained carbon and hydrogen and generally oxygen, also very frequently nitrogen, and occasionally sulphur and phosphorus. Moreover, bodies entirely different in chemical and physical properties might yet contain the same set of elements. Acetic acid, alcohol, sugar, starch, animal fat, vegetable oils, glycerin, etc., contain the same three elements—carbon, hydrogen, and oxygen. It was inconceivable that such differences in character could be evolved out of the same three elements without the intervention of some special power, and this was termed "vital force." The living world, so it was held, laid aside the rules which governed inorganic chemistry. It possessed its own laws of combination and its own force of affinity. These views proved to be entirely illusory. For it was not long before organic compounds were found to obey the same simple laws of combination by which inorganic chemistry was governed.

And here reference must be made to the important rôle which accurate analytical methods have played in consolidating the foundation upon which this new branch of chemistry was erected. It was Berzelius who in 1814, by improving the method of analysis, was able to prove that at least the simpler organic acids consisted of elements united in simple atomic proportion. A still more accurate and easy analytical process, which was devised by Liebig in 1830 and is still used in all its essential details, only served to confirm this interesting result (p. 14).

But the belief in a " vital force " was not so easily eradicated. On the appearance of the first artificial products, hitherto derived from natural sources, it began to lose ground. Oxalic and formic acids, alcohol, and urea were prepared in the laboratory.

The most remarkable of these four investigations is undoubtedly the production of urea, a substance associated with waste products of the animal economy, which was first prepared artificially by Wöhler in 1828.

Organic synthesis, as it is called, broke down the last barrier which separated the products of the organic from the inorganic world of matter.

Although many of the more complex natural products have not yet been obtained artificially, there is a sufficient array of these substances to warrant the firm belief that what the living animal or plant has accomplished within its own hidden workshop may be imitated by the chemist in his laboratory.

Among synthetic compounds which fifty years ago were exclusively of natural origin may be mentioned oil of bitter almonds, grape sugar and fruit sugar, alizarin and indigo, caffeine, camphor, and limonene (contained in oil of lemons, etc.), uric acid (found in the excreta of reptiles), conine from hemlock, cocaine from the coca leaf, and many others.

Thus, organic chemistry has renounced its original meaning, and now takes its place as one chapter—a very large one—in the science of chemistry, which treats of **the compounds of carbon.**

Let us look a little more closely into the subject of chemical synthesis, which may be said to be one of the ultimate aims of the organic chemist. The organic chemist finds a powerful and valuable vegetable drug like quinine, which is costly on

account of the comparatively small quantity present in the cinchona bark from which it is extracted, or an important dye-stuff like indigo, which is grown in the East and has to be imported into Europe from a distance of thousands of miles. How is he to set about building up these substances from simpler and cheaper materials in the laboratory? He cannot do it directly. He must first discover the elements of which the substance to be synthesised is composed, then the *relative number* of atoms of each element present; thirdly, he must find the weight of the molecule, or, in other words, the *actual number* of each kind of atom.

All this is comparatively easy, and merely involves a knowledge of analytical and other recognised methods of procedure, which will be presently explained. The next stages are more difficult, for he must proceed to break up his molecule bit by bit by lopping off groups of atoms until he has so far simplified his molecule as to be able to identify the residual nucleus. This nucleus then becomes his starting-point in the synthetic process, and his task now consists in piecing together the portions he has detached. In this way, if he is successful, he will finally obtain the product from which he started.

But he may be confronted with a difficulty, the cause of which was only slowly recognised by the earlier investigators. He may piece together the separate parts of his molecule and obtain a substance which contains the same elements and the same number of atoms of each as the original substance, and yet the two may be unlike. How is this to be explained? Sulphuric acid is written H_2SO_4, and no other substance possesses this formula; but C_2H_6O stands, not for one, but for two substances, whilst $C_8H_{12}O_4$ represents 66 different compounds. What does this imply? Simply that the atoms may be differently grouped. It is clear also that the larger the number of atoms in the molecule, the greater the possible variety of combinations. Thus, in the example given, the bigger molecule offers the larger number of variations.

Compounds of this character which have the same number and kind of atoms are said to be **isomeric.** This phenomenon of **isomerism** is a feature of organic synthesis which constantly

presents itself. It follows that, before a successful synthesis can be accomplished, the position of every atom must be ascertained, so that the production of an isomeric substance may, as far as possible, be avoided. The grouping of the atoms in a molecule is known as its **structure** or **constitution**. The study of structure necessarily precedes that of synthesis.

PART I

GENERAL PRINCIPLES

CHAPTER I

THE PURIFICATION OF ORGANIC COMPOUNDS

BEFORE the structure of any compound can be ascertained it is necessary to have it in a state of purity—that is, to remove every foreign ingredient. We will begin, then, by inquiring a little more closely into the way in which a compound may be purified. The majority of solid organic compounds are crystalline, and the method of purifying such substances is usually by the process of crystallisation. The impurities commonly remain in the mother liquor.

Crystallisation.—The first essential is to select a suitable solvent, that is, one which dissolves much more of the substance at a high than at a low temperature, or to use two miscible solvents, in one of which, however, the substance is but slightly soluble. We may make use of the latter method for crystallising cane-sugar, which is soluble in water but nearly insoluble in alcohol.

EXPT. 1.—**Purification of Cane-sugar.**—Dissolve in a small beaker 8 grams of cane-sugar in 4–5 c.c. of water by warming gently, add 20 c.c. of alcohol to the solution, shake up and drop in a small crystal of sugar. Let the solution stand till next day. The cane-sugar is deposited in crystals. Brown sugar may be purified by first removing the colour with animal charcoal and

then crystallising. Boil over a small flame 8 grams of brown sugar dissolved in 40 c.c. of water with the addition of about a gram of animal charcoal for a quarter of an hour. The liquid loses its brown colour. Filter and evaporate in a basin until about 10 c.c. of liquid are left. Pour into a beaker, add 20 c.c. of alcohol, and if a precipitate is formed, cautiously add water drop by drop until, on warming, a clear solution is obtained. Put in a crystal of sugar and leave overnight covered with a watch-glass. Colourless crystals of cane-sugar separate.

Melting-point determination.—The majority of solid organic compounds fuse when heated. This is an important property,

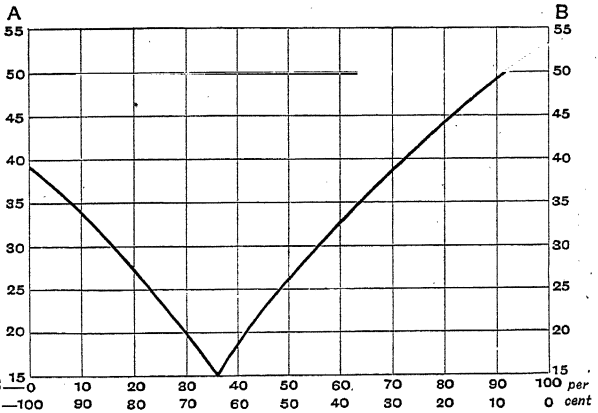


FIG. 1.

for by its means the purity of a compound may be ascertained. It is well known that the presence of a "foreign ingredient" lowers the melting point of a substance. Fusible metals are made on this principle. If we made various mixtures of two substances A and B and plotted their melting-points as ordinates and the quantities as abscissæ we should obtain a curve something like that in the accompanying Fig. 1. The melting-point of each would fall with successive additions of the second substance until it reached a minimum and would then rise until the second pure substance alone was present.

Successive crystallisations would show by a change or other-

wise in melting-point if the substance were pure. Slow liquefaction is usually an indication that the substance is impure or decomposes for the following reason: on cooling a mixture of two substances, the one that predominates would separate until the mixture of minimum melting-point (eutectic point) is attained, when the whole would solidify. On heating a mixed solid the reverse occurs, and if the process takes place slowly some of the more fusible mixture will melt, leaving the purer and therefore the substance with the higher melting-point. Thus the melting is protracted and may take place through a wide range of temperature.

EXPT. 2.—**Melting-point of Cane-sugar.**—For melting-point determinations the following method is used. A small sample of finely powdered cane-sugar, which has been carefully dried, is introduced into a capillary tube of about 1 mm. inside diameter sealed at one end. The tube is made from soft thin-walled glass tubing, about 15 mm. diameter, by rotating it in the blow-pipe flame until the glass softens, and then slowly drawing it out. The long capillary is then broken into lengths of about 7 cm. (2½ in.) by scratching across with a writing diamond, and each short tube is sealed at one end. To introduce the substance, it is convenient to scoop up the finely powdered material off a watch-glass with the open end. By tapping the closed end on the bench, the powder is shaken down. The quantity introduced should occupy a length of about 2–3 mm. when tightly packed. The tube is attached to a thermometer (preferably with a very small bulb) so that the substance is level with the bulb. The attachment may be made by a narrow rubber ring or by simply moistening the side of the capillary with the thermometer bulb, which has been dipped in the liquid in the bath, and then pressing it against the thermometer stem.

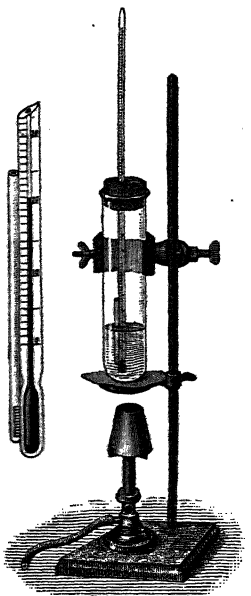


FIG. 2.—Apparatus for determining the melting-point.

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The thermometer passes through a cork loosely inserted into a large test-tube (boiling-tube) filled with concentrated sulphuric acid, glycerin or castor oil to a depth of about 5 cm. (2 in.). The apparatus is clamped to a retort stand over wire gauze and is heated very gradually by a small flame. When a certain temperature is reached the substance, if pure, melts suddenly within one or two degrees. When approaching the melting-point, it is desirable to remove the flame or turn it very low so that the rise of temperature is very gradual. If the liquefaction is protracted, it is an indication that the substance is not pure. The melting-point, obtained in this way, to be quite accurate, must be corrected for the temperature of the thread of mercury outside the liquid.

Some substances do not melt, but, on reaching a certain temperature, decompose. The purity of such substances can only be approximately gauged by repeated crystallisation and careful microscopic examination. It is difficult to establish with certainty whether substances such as resin, starch, and albumin, which do not crystallise, are single individuals or not, and purification is rendered very troublesome.

PREPARATION AND PURIFICATION OF ETHYL ALCOHOL

Fermentation.—When brewers' yeast (saccharomyces) is added to a solution of grape-sugar (glucose) or cane-sugar, the liquid shortly begins to froth and has the appearance of boiling, although there is a scarcely perceptible rise of temperature. The process is called fermentation, from the Latin *fervere* to boil. A fundamental change occurs in the sugar, whereby it is broken up into **ethyl alcohol** and carbon dioxide.

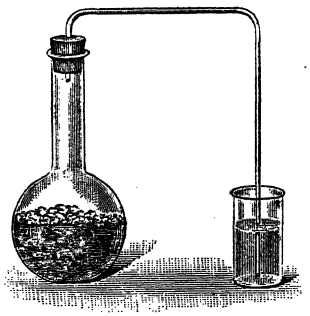


FIG. 3.—Fermentation of a sugar solution.

EXPT. 3.—Dissolve 50 grams of grape-sugar (glucose) in 500 c.c. of water; pour the solution into a large flask (2 litres), and add about half an ounce of fresh brewer's yeast. Fit the flask with a cork and bent delivery tube, dipping into lime-water (Fig. 3).

Warm the solution to about 25°–30° C.,[1] and leave the flask in a warm place. After a short time bubbles of gas appear, and a considerable deposit of calcium carbonate will form in the lime-water. After two days the presence of alcohol in the flask may be ascertained by pouring out a small portion of the liquid into a flask furnished with an upright tube. On gently boiling the contents, the vapour of alcohol, which is more volatile than water, is the first to pass out of the open end of the upright tube, and may be ignited. The remaining contents of the flask are distilled.

Fractional distillation.—To separate the alcohol from the other contents of the liquid and to some extent from water,

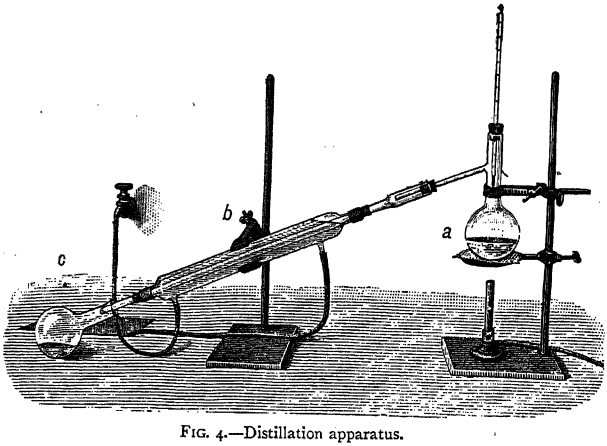


FIG. 4.—Distillation apparatus.

recourse is had to the process of fractional distillation. The apparatus is shown in Fig. 4. It consists of a distilling flask, *a*, a condenser, *b*, and a receiver, *c*. The flask is provided with a thermometer which is inserted through a cork in the neck. If the liquid in *a* is boiled the vapour passes into the inner tube of the condenser, where it is cooled by a current of cold water in the manner indicated, and the condensed liquid runs into the receiver, *c*. This process is called distillation and the temperature of the vapour of the boiling liquid, as indicated by the thermometer, is the *boiling-point* of the liquid. It will be found, however, that, as the liquid distils, the thermometer shows a

[1] As temperatures are always referred to the centigrade scale, the "C" will henceforth be omitted.

gradual rise of temperature. This is due to the fact that two liquids are distilling, alcohol boiling at 78° and water at 100°. The boiling-point curve of an alcohol and water mixture will be represented by a continuous line rising from pure alcohol at 78° to pure water at 100° (Fig. 5).

It follows, therefore, that every portion distilling will consist of an alcohol and water mixture containing, as the temperature rises, an increasing proportion of water.

It may be added that certain mixed liquids exhibit concave and others convex boiling-point curves, that is, a certain mixture has a

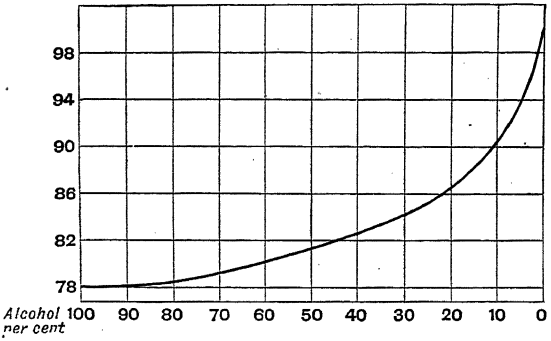


FIG. 5.—Boiling-point curve of alcohol and water mixtures.

boiling-point which is either higher or lower than either of the pure substances. This method of separation is then less easily applied.

By collecting the first portion or fraction of the distillate which boils below 100° (about 50 c.c.) a partial separation is effected. This fraction will contain the main portion of the alcohol. The process of separating the distillate into fractions of different boiling-points is called **fractional distillation** and is employed in many large technical operations such as the petroleum industry (p. 83), the destructive distillation of wood (p. 54), and of coal (p. 246) and in spirit distilleries (p. 23).

A more effective method for separating the alcohol by distillation is to use a column or still-head. There are many forms of this apparatus, one of which is made from a piece of wide tubing of about 15 mm. inside diameter drawn out below or sealed to a narrower piece of tubing at the lower end and filled with thin glass beads, kept in position by plugs of copper gauze. The upper end is fitted with a T-piece holding the thermometer

as shown in Fig. 6, *b*. It is known as a Hempel column. Another form of column (Vigreux column) can be made from a similar piece of wide tubing by heating it at various points with the tip of a narrow blow-pipe flame until soft, and inserting the end of a file with a slight pressure inwards. A ring of three or four such indentations is made so that the projections inside nearly touch, and at intervals of about $1\frac{1}{2}$–2 inches as in Fig. 6, *a*.

The action of the column may be explained as follows. The vapour given off from a mixture of liquids contains, as a rule, a larger proportion of the more volatile constituent than the liquid. If this vapour is partly condensed in its ascent, the vapour above this condensed liquid will be still richer in the more volatile constituent. If, by a series of constrictions or diaphragms, the condensed liquid is obstructed in its return flow, a momentary equilibrium between liquid and vapour is established at each diaphragm, and the longer the column the greater will be the amount of the more volatile constituent in the last portion of vapour to undergo condensation. This passes off by the condenser and is collected.

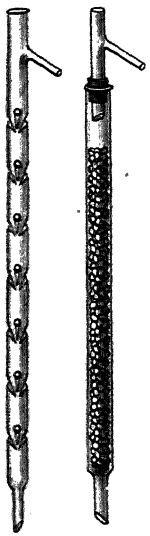


FIG. 6.—Fractionating columns.

The alcohol partially separated in this way still contains water. A more complete separation could be effected by a second fractional distillation within a narrower range of temperature; but this may be omitted. The remaining water can be removed by adding a quantity (about 20 grams) of solid potassium carbonate to the 50 c.c. of distillate. The carbonate absorbs the water and forms a heavy liquid layer below the layer of alcohol. The lower layer is removed by means of a pipette, or more conveniently by means of a tap-funnel (Fig. 7).

The alcohol is further dehydrated with fresh potassium carbonate or quicklime. If the alcohol is now separated from the solid and distilled, the liquid will show a nearly constant boiling-point of 78°–79° throughout the distillation. The constancy of boiling-point is an indication of purity. The quantity obtained in this way is usually about 20 c.c.

Composition of Sugar and Alcohol (qualitative).—The method for ascertaining the presence of carbon and hydrogen in organic compounds will now be described. In the case of the less volatile and non-inflammable substances, the compound is mixed with copper oxide and heated. The carbon is converted into carbon dioxide and the hydrogen into water, the copper oxide being at the same time reduced to the metal.

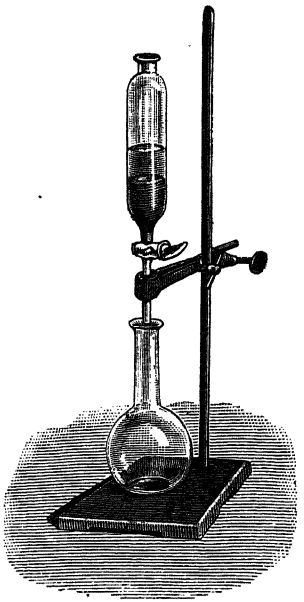


FIG. 7.—Tap-funnel for separating non-miscible liquids.

EXPT. 4.—Fit a small hard glass test-tube with cork and delivery tube dipping into lime-water (Fig. 8). Heat a few grams of fine copper oxide in a porcelain crucible for a few minutes to drive off moisture, and let it cool in a desiccator. Mix it with about one-tenth of its bulk of powdered sugar in a mortar. Pour the mixture into the tube. Clamp the tube horizontally to a retort stand and tap it gently so as to leave a channel along the top for the escape of gas. Heat the mixture gently with a small flame. The gas which bubbles through the lime-water turns it milky. Moisture will appear near the cork, and, provided that the copper oxide has been thoroughly dried beforehand, this indicates the presence of hydrogen in the compound.

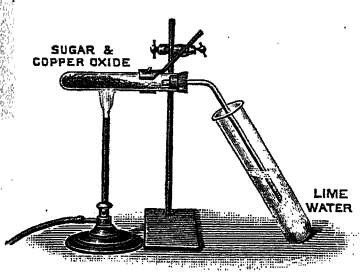


FIG. 8

The presence of carbon and hydrogen in alcohol or other inflammable liquid is determined by burning the substance and testing for carbon dioxide and water.

EXPT. 5.—Place a little alcohol in a deflagrating spoon and burn it in a dry jar. Notice the deposition of moisture on the sides of the jar. On shaking the vessel after the addition of lime-water, the latter becomes turbid. The formation of water and carbon dioxide shows the presence of carbon and hydrogen. There is no convenient qualitative test for oxygen.

Quantitative analysis of carbon compounds.—The method used to determine quantitatively the composition of organic compounds consists in burning in a current of oxygen a weighed amount of the substance (unless it is a gas, when a different method is employed) in a tube containing copper oxide. The hydrogen forms water (H_2O), and the carbon is converted into carbon dioxide (CO_2). Each of these is separately absorbed in a weighed apparatus. The water is collected in a tube containing pieces of calcium chloride, which takes up moisture with

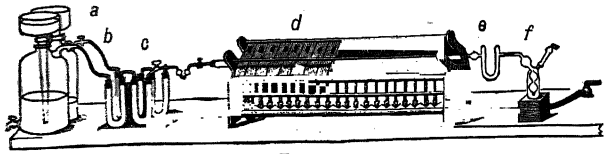


FIG. 9.

great avidity, and the carbon dioxide in a small vessel consisting generally of two or three bulbs filled with caustic potash solution, which absorbs the gas. The apparatus is shown in Fig. 9.

Oxygen is introduced from the reservoir or gas holder *a*, and is purified by passing through tubes *b* and *c*, containing respectively soda-lime and strong sulphuric acid, to remove traces of carbon dioxide and moisture. The weighed substance is placed in the tube in a little boat at *d*, and the rest of the tube is filled with copper oxide. The object of the copper oxide (CuO) is to oxidise the substance which may come into contact with it, as already explained. The tube, filled in the manner described, is attached to the calcium chloride tube *e*, and to the bulb apparatus *f* containing caustic potash, both of which are carefully weighed. The long tube is heated gradually in the furnace by means of a series of gas burners, whilst a current of oxygen is slowly passed through, and thus helps to burn the substance and at the same time carries

along the products (water and carbon dioxide) into the two vessels *e* and *f*, in which they are absorbed. A second gas holder containing air is used for replacing the oxygen in the apparatus *e* and *f* by air at the end of the operation. These two vessels are then weighed and the quantity of water and carbon dioxide ascertained. We know from previous experience that $\frac{2}{18}$ths or $\frac{1}{9}$th part by weight of water is hydrogen and $\frac{12}{44}$ths or $\frac{3}{11}$ths by weight of carbon dioxide is carbon. Thus, from the increase in weight of the two vessels we can find the weight of carbon and hydrogen in the substance.

Example.—0·2 gram of grape-sugar produced 0·294 gram of carbon dioxide and 0·120 gram of water.

Hence,

$\frac{3}{11} \times 0{\cdot}294 = 0{\cdot}080$ gram of carbon.
$\frac{1}{9} \times 0{\cdot}120 = 0{\cdot}013$,, hydrogen.

To convert these into parts per cent. multiply by 100 and divide by the amount of substance taken. The difference between the sum of these two quantities and 100 must be due to oxygen.

$\frac{100 \times 0{\cdot}080}{2} = 40{\cdot}0$ per cent. of carbon.

$\frac{100 \times 0{\cdot}013}{2} = 6{\cdot}5$,, hydrogen.

difference $= \underline{53{\cdot}5}$,, oxygen.
$100{\cdot}0$

If these numbers are now divided by the respective atomic weights of the elements, the *relative* (not the actual) numbers of atoms present in the molecule are given.

$\frac{40}{12} = 3{\cdot}3$ atoms of carbon.

$\frac{6{\cdot}5}{1} = 6{\cdot}5$,, hydrogen.

$\frac{53{\cdot}5}{16} = 3{\cdot}3$,, oxygen.

Dividing by the smallest number so as to give the proportion in whole numbers, we get approximately CH_2O. This is known as the **empirical formula,** because it does not tell us the absolute number of such atoms, which is given by the **molecular formula.** In the same way, the empirical formula for ethyl alcohol would be found to be C_2H_6O.

Molecular weight and molecular formula.—In order to find the weight of the molecule, or molecular formula, we make use of certain hypotheses. One is called **Avogadro's hypothesis,** which states that equal volumes of gases under similar conditions contain an equal number of molecules. Therefore the relative weights of equal volumes (or density) will be the relative weights of their molecules.

For example, supposing each of the circles, Fig. 10, represents an equal volume of hydrogen and of some other gas, *x*, according to Avogadro's hypothesis they contain the same number of molecules; let us say four. It is clear that if we compare the weights of these two volumes, we are really comparing the weights of their individual molecules. Now the weight of a given volume of vapour compared with that of an equal volume of hydrogen is the **vapour density,** or,



FIG. 10.

$$\text{vapour density} = \frac{\text{weight of } x}{\text{weight of hydrogen}}$$

It is a very easy matter to weigh a certain volume of a gas or vapour (*i.e.* gasified liquid or solid) which is not changed chemically by heating. Furthermore, we know from exact determinations what the weight of any volume of hydrogen is at any temperature or pressure (1 c.c. = 0·00009 gram at 0° and 760 mm.). Thus we can find what the weight of the molecule of the substance is compared with a molecule of hydrogen. But the molecule of hydrogen is supposed to consist of two atoms, and as we take the single atom of hydrogen (being the lightest substance known) as the unit for comparison, we have to multiply the above result by two. This gives the weight of the molecule of the substance compared with one atom of hydrogen, which is what we mean when we speak of **molecular weight.** This method is called **vapour density method,** and may be carried out in various ways. One of these is known as Victor Meyer's air displacement method. The apparatus and procedure are described in detail in Expt. 20 under *ether* (p. 42). The vapour density of alcohol compared with hydrogen under the same conditions of temperature and

pressure would be found to be 23 and therefore the molecular weight of alcohol is $2 \times 23 = 46$, which is that given by the formula C_2H_6O.

This method cannot of course be used for a non-volatile solid, such as cane-sugar, and consequently another method has to be adopted. The method depends upon the fact, first demonstrated by Raoult, that the freezing-point, and also the boiling-point, of a substance is changed (lowered in the first case and raised in the second) by the same number of degrees by dissolving in it different substances whose weights are proportional to their molecular weights. This result is due to the change effected in the vapour pressure of the solvent by the dissolved substance. Supposing we plot the change in vapour pressure with temperature for ice and water in the form of a curve, and then do the same after dissolving in it a small quantity of substance. The new curve will run nearly parallel with the first (Fig. 11). It will cut the vapour pressure curve for ice at some point below 0° and reach atmospheric pressure above 100°; in other words, the addition of a soluble substance will lower the freezing-point and raise the boiling-point. Not only so, but if an equal molecular proportion of another substance were dissolved in the same quantity of water, precisely the same effect would be observed.

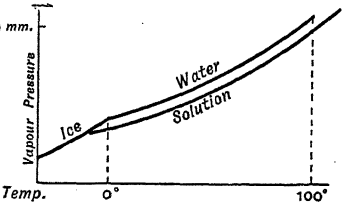


FIG. 11.

The freezing-point method.—Supposing the freezing-point of 100 grams of a solvent to be lowered 1° by dissolving 1, 2, 3, and 4 grams respectively of four different substances, the molecular weights of these substances will be in the ratio of 1 : 2 : 3 : 4. In order to convert these ratios into true molecular weights, the numbers must be multiplied by a coefficient which depends upon the nature of the particular solvent selected, and which may be determined empirically by means of substances of known molecular weight or by calculation from thermodynamical data.[1]

[1] Reference should be made to a book on physical chemistry for further details.

If w is the weight of substance and W the weight of solvent, d the depression of the freezing-point, and C the coefficient for the solvent determined for the standard conditions (*i.e.* for the weight of substance which produces 1° depression in 100 grams of solvent) the molecular weight, M, is given by the following expression :—

$$M = \frac{100\,Cw}{dW}.$$

The values of C for the common solvents in use are as follows :—

Water	18·8,	Phenol	75,
Benzene ..	50,	Acetic acid ..	39.

The form of apparatus, known as the **Beckmann freezing-point apparatus,** is shown in the accompanying Fig. 12. It consists of a glass jar furnished with a stirrer. The cover of the jar has a wide slit to admit the stirrer, and a circular aperture with clips to hold a wide test-tube.

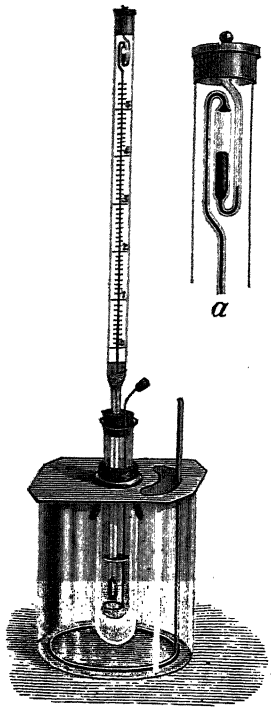


FIG. 12.—Beckmann's freezing-point apparatus.

Within the wide test-tube is a narrower one, which is held in position by a cork. The narrow test-tube is sometimes furnished with a side-tube for introducing the substance. It is provided with a stirrer. A Beckmann thermometer completes the apparatus. This is fixed through a cork so that the bulb nearly touches the bottom of the tube, a wide slit being cut in the side of the cork for moving the stirrer. The Beckmann thermometer is of special construction, and requires explanation. As the method involves merely an accurate determination of small differences of temperature, it is not requisite to know the exact position on the thermometer scale. The Beckmann thermometer registers 6 degrees, which are divided into

hundredths. The little glass reservoir at the top (*a*, Fig. 12) serves the purpose of adjusting the mercury column to different parts of the thermometer scale by adding or removing mercury from the bulb. Ten to fifteen grams of solvent are introduced into the inner tube and weighed. The freezing-point of the solvent is then determined by cooling the outer vessel with water, ice, or a freezing mixture of powdered ice and salt, below the freezing-point of the solvent. The solvent is slightly supercooled and then stirred. As soon as crystals begin to separate, the temperature rises, and reaches a maximum which represents the freezing-point of the solvent. The operation is repeated for confirmation, and then a carefully weighed amount of the substance introduced. As soon as the substance has dissolved, the freezing-point is again determined as before, and this time a lower temperature will be indicated. A further quantity of substance may be added, and a new determination made.

Example.—Using 1 gram of cane-sugar in 15 grams of water, the freezing-point was lowered 0·37°.

The molecular weight is calculated as follows: it is first necessary to find the weight of substance which when dissolved in 100 grams of solvent will lower the freezing-point 1°.

The weight of substance w in 100 grams of solvent is given by the expression:

$$\frac{1 \times 100}{15}.$$

As the proportion between the substance and the solvent is unchanged, no effect is produced on the freezing-point.

The weight of substance in 100 grams of solvent required to lower the freezing-point 1° is

$$\frac{1 \times 100}{15 \times 0{\cdot}37}.$$

Here it is assumed that the depression of the freezing-point is proportional to the weight of dissolved substance.

The above factor multiplied by the coefficient for the solvent (water = 18·8) gives the molecular weight.

$$\frac{1 \times 100 \times 18{\cdot}8}{15 \times 0{\cdot}37} = 338.$$

The molecular weight calculated for $C_{12}H_{22}O_{11} = 342$.

The boiling-point method.—The boiling-point of a liquid is found to be affected like the freezing-point by the presence of a dissolved substance—that is, the boiling-point of a given quantity of a liquid is *raised* the same number of degrees by dissolving in it the same number of molecules of different substances, or, in other words, such weights of these substances as represent the ratio of their molecular weights. One form of apparatus for determining molecular weights by this method is that of Beckmann, shown in Fig. 13.

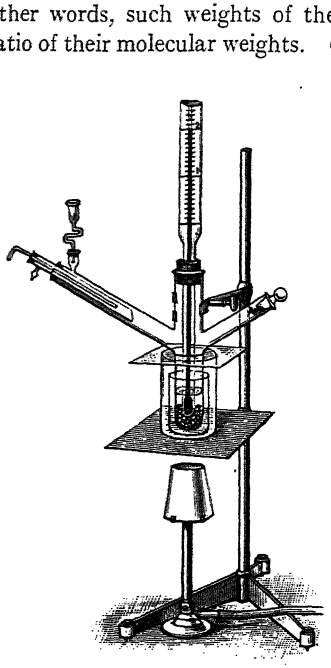


FIG. 13.

Beckmann's boiling-point apparatus consists of a boiling-tube furnished with two side-pieces, one of which is stoppered and serves to introduce the substance, and the other acts as a condenser. The boiling-tube stands on an asbestos pad and is surrounded by two short concentric glass cylinders surmounted by a mica plate. A Beckmann thermometer is inserted through a cork in the neck of the tube. The thermometer is similar in construction to that used for freezing-point determinations, but it has a smaller bulb. The boiling-point of the solvent is first ascertained. The burner is lighted and the temperature regulated so that the liquid boils briskly. The temperature being constant, it is noted, and a weighed pellet of the solid substance is dropped into the boiling-tube through the side-piece without interrupting the boiling. The boiling-point rises, and after a short time will remain stationary. The temperature is again noted. A second and third determination may be made by introducing fresh pellets of the substance.

When the observations are complete, the apparatus is allowed o cool and the weight of solvent ascertained by weighing the oiling-tube and solvent.

As in the freezing-point method, the molecular weight is calcu- ated from the weight of substance required to raise the boiling- oint of 100 grams of solvent 1°, and the result multiplied by a oefficient which depends upon the nature of the solvent. The llowing is a list of solvents commonly employed and their oefficients and boiling-points :—

	b.-p.	*c.*		b.-p.	*c.*
cetone	56°	17·1	Ethyl alcohol ..	78°	11·5
hloroform ..	61°	36·6	Benzene	80°	26·1
ethyl alcohol ..	66°	8·8	Water	100°	5·2
thyl acetate ..	77°	26·8	Acetic acid ..	118°	25·3

The molecular weight is determined from the formula

$$M = \frac{100\,cw}{dW},$$

which w is the weight of substance, W that of the solvent, the rise of boiling-point, and c the coefficient.

Although the method is able to dispose of a greater number of nvenient solvents than are adapted for freezing-point deter- nations, it is never so accurate, mainly on account of the diffi- lty of avoiding fluctuations in the boiling-point, due to radiation, the dripping of cold liquid from the condenser, and to baro- tric fluctuations.

Example.—With 4·5 grams of cane-sugar in 15 grams of water e boiling-point was raised 0·48°.

$$M = \frac{100 \times 4{\cdot}5 \times 5{\cdot}2}{15 \times 0{\cdot}48} = 325.$$

Having now settled the formula for alcohol the most important k remains—that of determining its structure or the arrange- nt of the atoms in the molecule.

Enzyme action.—Before studying the structure of alcohol, will refer for a moment to the process by which the alcohol obtained from sugar.

the French chemist Lavoisier.

$$\underset{\text{Grape-sugar.}}{C_6H_{12}O_6} = \underset{\text{Ethyl alcohol.}}{2C_2H_6O} + \underset{\text{Carbon dioxide.}}{2CO_2}$$

Now, although this represents the main result of the process, it is not the only one; for it is found that other alcohols, containing three, four, and five carbon atoms, are produced in smaller quantities at the same time (p. 107), namely:—

	Boiling-point.
Propyl alcohol, C_3H_8O	97°
Butyl alcohol, $C_4H_{10}O$	107°
Amyl alcohol, $C_5H_{12}O$	132°

These can be separated by fractional distillation; the higher boiling portion, consisting mainly of amyl alcohol, is known in trade as **fusel oil.**

Let us consider for a moment how the yeast effects this curious change. It has been stated that yeast is a living organism. It consists of a large number of single microscopic spherical cells, about $\frac{1}{1000}$ in. in diameter. Each of these cells multiplies by budding, and forms a new cell which ultimately becomes detached from the parent cell, and thus the process continues with great rapidity. Moreover, as Pasteur proved, it is only in presence of living yeast that fermentation can proceed. If the yeast is killed by boiling the liquid, or removed by filtration, fermentation ceases. In what manner, then, does the living cell act? A partial answer to the question has been given by the German chemist, Buchner, who was able by using great pressure on the dried and ground yeast to squeeze out a yellowish liquid which could induce fermentation like the living cell. It follows, therefore, that the living yeast cell secretes a liquid which brings about the change, and that it is a chemical as distinguished from a vital process. The liquid is called **zymase.**



FIG. 14.—Yeast cells (highly magnified).

Enzymes.—Without giving a complete answer to the question as to how the sugar is converted into alcohol, we can affirm that

covery seems indeed to point to the probability that all vital functions have a chemical basis. We know many examples of animal and vegetable substances producing rapid chemical changes outside the living body. They usually contain nitrogen, and are soluble in water. They are known as **enzymes**, and evidently play a conspicuous rôle in animal and plant life.

Among the commoner of the enzymes are **diastase**, which occurs in green leaves and germinating grain, and converts starch into sugar (p. 160); **ptyalin**, a similar and probably identical body found in the saliva; **pepsin** and **trypsin**, which are concerned in the digestive process, and many others.

The manufacture of beer, wines, and spirits.—We will now consider very briefly the manufacture of alcoholic beverages, which depend upon fermentation.

In the brewing of beer, barley, which like most cereals contains a large amount of starch, is soaked in water and spread out on extensive floors. Germination soon begins, and is allowed to proceed until a small shoot appears, when the life of the grain is destroyed by heating in kilns, known as malt-kilns. The product, which retains the appearance of the original grain, is called **malt.** One object of germination is to produce the enzyme **diastase**, so that when the malt is placed in warm water the diastase may act upon the starch, which it rapidly converts into sugar. The sugar is similar in some respects to cane-sugar, but is a different substance and is known as **malt-sugar** (p. 160). In the brewing of beer the action of the diastase is arrested after a short interval, so that only a small proportion of the starch is converted, and the extract or **wort** is drawn off and run into large copper pans and boiled with the addition of hops. The hot liquid is rapidly cooled and placed in stone vats. Yeast is added, whereupon fermentation sets in, and the sugar is converted into alcohol. The product is **beer.** If all the starch in the malt is converted into sugar and fermented, a material results which is naturally much richer in alcohol; and if this is distilled, so as to separate the alcohol and water from the other ingredients in the liquid, then **whisky** results. **French brandy**, in the same way, is made by distilling the alcohol from wine. **Rum** is the distillate from fermented molasses;

gin, like whisky, is made from barley and flavoured with juniper; the Japanese wine **sake** is made from fermented rice. **Wine** is made from grape-juice, which is allowed to ferment, and the sugar which the grape contains is thus converted into alcohol.

If pure alcohol is required, an alcoholic liquid is prepared by adding malt to unmalted grain or to potatoes, which are rich in starch, whereby the latter is converted into sugar, and after fermentation the alcohol is separated from the residual grain and, so far as possible, from water, by fractional distillation in large stills, after which it is freed from water by standing over quicklime. After a final distillation over quicklime it is known as **absolute alcohol.** Pure ethyl alcohol is a colourless liquid with a burning taste, which boils at 78°. All alcoholic liquids and substances manufactured from alcohol pay a Government tax at the rate of ten shillings a gallon of **proof spirit**—that is, a spirit consisting approximately of half alcohol and half water by weight, and all alcoholic liquids pay *pro rata* on the proportion of alcohol they contain. This proportion is determined by means of a special hydrometer (Sikes) and tables of specific gravities. The following table gives the approximate content of alcohol usually found in different beverages.

	Per cent.		Per cent.
Whisky	40	Burgundy	13
Brandy	40	Hock	9
Rum	40	Claret	7
Gin	35–40	Ale	6
Port	20	Porter	5–6
Sherry	16	Munich beer	4–5

In determining the alcohol in beer and wine which contain other materials in addition to alcohol and water, a certain volume of the liquid is distilled so as to remove all the alcohol, and the distillate is then made up to the original volume and its specific gravity determined.

In the United Kingdom about 170 million pounds' worth of alcoholic liquids are consumed annually, which contribute in duty about 30 to 40 millions sterling to the revenue of the country.

Methylated spirit, which, by the addition of wood spirit (p. 24) to spirits of wine in the proportion of 1 volume of the former to

9 volumes of the latter, renders the spirit unfit for consumption, pays no duty, and is used very largely in trade as a substitute for pure ethyl alcohol.

Ethyl alcohol is usually detected by what is known as the *iodoform test.*

EXPT. 6.—**Iodoform test.**—To a few drops of alcohol add about 10 c.c. of the ordinary solution of iodine in potassium iodide and then caustic soda until the brown colour just disappears. Warm very gently for a minute. A turbidity soon appears, and on standing minute yellow crystals of iodoform, CHI_3, are deposited, which, under the microscope, appear as hexagonal stars or plates. Iodoform has a peculiarly unpleasant smell (see p. 103).

QUESTIONS ON CHAPTER I.

1. How do you purify and determine the purity of (1) a crystalline solid, (2) a volatile liquid ?

2. Explain by means of an imaginary melting-point curve why an impure substance shows gradual fusion.

3. How would you show that alcohol contains carbon and hydrogen ?

4. Calculate the percentage composition of cane-sugar $C_{12}H_{22}O_{11}$ and grape-sugar $C_6H_{12}O_6$.

5. Calculate the percentage of carbon, hydrogen, and oxygen from the following data : 0·2046 gram of substance gave on combustion 0·2985 gram of CO_2 and 0·1255 gram of water.

6. How would you prepare a specimen of pure alcohol from glucose ?

7. Calculate the molecular weight of grape-sugar, determined by the freezing-point method from the following data : 1 gram of substance in 14·62 grams of water lowered the freezing-point 0·725°, $c=18·8$.

8. Given a non-volatile, neutral, solid organic compound, how would you proceed to determine its molecular weight ?

9. The following result was obtained by the boiling-point method in alcohol. Calculate the molecular weight : 1·01 grams of substance in 24·2 c.c. of alcohol raised the boiling-point 0·535°. The specific gravity of alcohol at the boiling-point is 0·7422, $c=11·5$.

10. A substance gave the following analytical result : C=54·5 ; H=9·09 per cent. ; O=difference. A vapour density determination by V. Meyer's method gave the following result : 0·1 gram of

substance displaced 27 c.c. of air measured at 15° and 745 mm. (vapour tension of water at 15°=12·7 mm.). Determine the molecular formula.

11. What is the effect of distilling a mixture of alcohol and water? Explain what happens.

12. Describe the steps by which alcohol may be prepared, starting with starch. What volume of air under normal conditions would have to be mixed with the vapour of 10 grams of alcohol to ensure complete combustion in an internal combustion engine?

13. Describe briefly the manufacture of beer, whisky, wine, and brandy. How would you propose to determine the presence and amount of alcohol which they contain?

CHAPTER II

SOME REACTIONS OF ETHYL ALCOHOL

THE structure of a substance is ascertained from a variety of reactions and the manner in which they may be interpreted. We will now study with this object some of the reactions for ethyl alcohol.

EXPT. 7.—**Preparation of Sodium ethoxide.**—Weigh out carefully in a well-corked tube 0·3–0·4 gram of clean cut sodium and fit up an apparatus shown in Fig. 15.

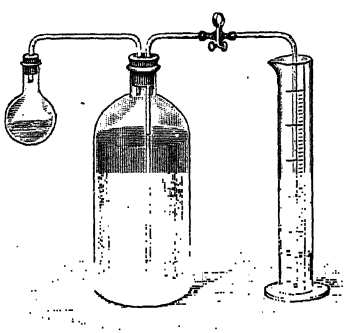


FIG. 15.—Measurement of the volume of hydrogen formed on dissolving a known weight of sodium in alcohol.

The Winchester quart bottle is filled with water and any air space left is removed by pouring a little water into the graduated cylinder (250 c.c.) and sucking the air out at the end of the tube to which the flask is attached. When the bottle is filled, the tube dipping into the cylinder should be full of water, and sufficient water should remain in the cylinder to cover the open end. When the pinch-cock is closed the level of water in the cylinder should remain stationary. Read off and note the level. Pour 10 c.c. of ethyl alcohol into the flask, drop in the weighed piece of sodium, attach the flask at once and open the cock. Effervescence occurs, due to evolution of hydrogen from the alcohol, and the sodium disappears. When action has ceased and the flask is cold, read off the level of the water in the cylinder. The difference gives the

volume of gas evolved. This should be reduced to normal temperature and pressure. The solution in the flask must now be evaporated to complete dryness on the water-bath.

Weigh a small basin with a short piece of glass rod. Pour the solution from the flask into the basin and rinse out the flask twice with a few c.c. of alcohol. Evaporate the liquid with constant stirring on the water-bath until dust-dry.

Cool in a desiccator and carefully and quickly weigh. This solid residue, which has a brown colour due to slight decomposition, is sodium ethoxide.

Example.—0·331 gram of sodium gave 182 c.c. of hydrogen at 19° and 758 mm. The vapour tension of water at 19° = 16 mm. The weight of 1 c.c. of hydrogen at 0° and 760 mm. = 0·00009 gram.

$$\frac{273 \times (758 - 16) \times 182 \times 0{\cdot}00009}{292 \times 760} = 0{\cdot}0149 \text{ gram of hydrogen.}$$

The residue on evaporation weighed 0·964 gram,

$$\frac{0{\cdot}964}{0{\cdot}0149} = 65^{1}$$

Therefore 1 gram of hydrogen is nearly equivalent to the molecular weight in grams of sodium ethoxide, or,

$$\underset{23}{Na} + \underset{46}{C_2H_6O} = \underset{68}{C_2H_5ONa} + \underset{1}{H}$$

It therefore follows that the one atom of hydrogen which is replaced is differently situated from the remaining five, seeing that it can be removed by sodium, whereas no amount of sodium will effect any change in the remaining hydrogen atoms.

EXPT. 8.—**Preparation of Ethyl chloride.**—Add a small quantity of phosphorus pentachloride to a few c.c. of alcohol. Notice the vigorous action and the evolution of fumes. The latter is due to hydrogen chloride, which may be identified by holding in the neck of the vessel a glass rod dipped in a solution of silver nitrate. At the same time, a new volatile organic liquid, ethyl chloride, is formed and also phosphorus oxychloride, which remain in the vessel. These products, which cannot be conveniently separated, point to the following reaction :

$$C_2H_6O + PCl_5 = C_2H_5Cl + HCl + POCl_3$$

[1] The low value is due to slight decomposition of the sodium ethoxide.

The same organic compound, ethyl chloride, is obtained by passing hydrogen chloride gas into hot alcohol in presence of solid zinc chloride, which takes up the water formed. The ethyl chloride, which boils at 12·5°, must be collected in a vessel cooled in ice.

$$C_2H_6O + HCl = C_2H_5Cl + H_2O.$$

Here it will be seen that an atom of hydrogen and oxygen have been replaced by one atom of chlorine. The fact that the two atoms are removed together might suggest some sort of union between them.

It is an interesting fact that if ethyl chloride is heated with water, especially if a base such as caustic soda or potash is present to remove the hydrogen chloride, ethyl chloride can be re-converted into the alcohol:

$$C_2H_5Cl + H_2O = C_2H_6O + HCl.$$

We therefore have two opposite reactions.

Can they both take place at the same time? They proceed together, or, in other words, neither reaction is completed; for if water is added to ethyl chloride, alcohol is formed, and as soon as the alcohol is formed some ethyl chloride is re-formed by the hydrochloric acid until a certain quantity of both is present, or they reach a state of equilibrium when we suppose that the opposing changes proceed at the same speed. The process is called **reversible**, and the result a **balanced action.** The balance or proportion of each depends upon various conditions and varies with the relative quantities at the beginning, and the temperature. If we desire only one reaction to take place, we must remove one of the products, and that is why we add caustic soda if the second reaction is to continue. If the first reaction is required, we add something which will remove water, such as zinc chloride, which absorbs it with great avidity.

Reversible reactions frequently occur among organic compounds where the substances are in solution together and these reactions are denoted by reversed arrows in place of the sign of equality thus:

$$C_2H_6O + HCl \rightleftarrows C_2H_5Cl + H_2O.$$

Hydrogen bromide and iod
and iodide by merely heating th
acid; but the following is a mor

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EXPT. 9.—**Preparation of Ethyl bromide.**—Ten grams of red phosphorus and 70 c.c. of ethyl alcohol are placed in a distilling flask, attached to a condenser and receiver. The receiver is connected with a soda-lime tower. A tap-funnel containing 20 c.c. of bromine is fixed through a cork in the neck of the distilling-flask. The apparatus is shown in Fig. 16. The flask is cooled in water and the bromine slowly added. The flask is then left for several hours, and the contents distilled on the water-bath. The soda-lime tower absorbs any fumes of hydrobromic acid which are evolved.

The distillate consists of ethyl bromide, which is purified by

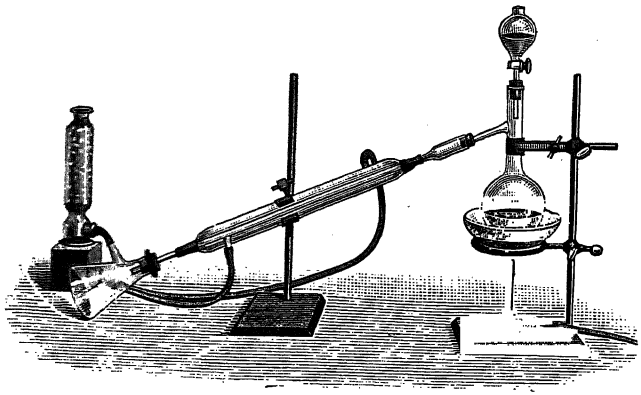


FIG. 16.—Preparation of ethyl bromide.

shaking it with a little sodium carbonate solution in a tap-funnel to remove both alcohol (which dissolves in the water) and hydrobromic acid (which combines with the sodium carbonate). The lower, and therefore heavier, insoluble layer is the ethyl bromide, which is withdrawn and separated from the water. It still contains a little water, which is removed by adding a few pieces of solid calcium chloride (dehydrating agent), and then re-distilling the liquid.

Ethyl iodide is prepared as above, using iodine in place of bromine. Ethyl bromide boils at 38°–39° and ethyl iodide at 72°.

The action of the phosphorus and the halogen is usually explained by supposing that PBr_3 and PI_3 are formed and that they react with the alcohol thus:

$$3C_2H_6O + PBr_3 = 3C_2H_5Br + H_2PO_3.$$

Alcohol also combines with other acids in addition to the halogen acids, such as nitric acid, to form **ethyl nitrate :**

$$C_2H_6O + HNO_3 = C_2H_5NO_3 + H_2O.$$

with sulphuric acid to form **ethyl hydrogen sulphate :**

$$C_2H_6O + H_2SO_4 = C_2H_5.HSO_4 + H_2O.$$

and with acetic acid to form **ethyl acetate :**

$$C_2H_6O + C_2H_4O_2 = C_2H_5.C_2H_3O_2 + H_2O.$$

These compounds of alcohol with acids or salts of the alcohols are termed *esters*.

EXPT. 10.—**Preparation of Potassium ethyl sulphate.**—Eighty c.c. of pure ethyl alcohol are poured into a round flask (250 c.c.) and

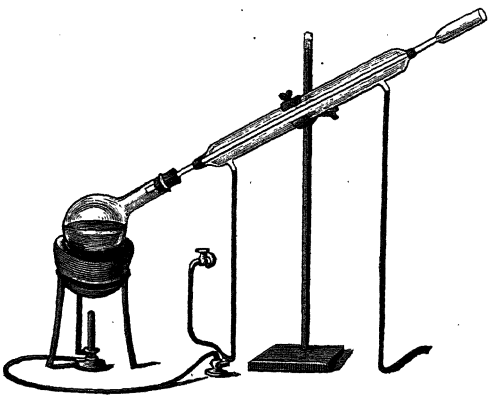


FIG. 17.

20 c.c. of concentrated sulphuric acid are slowly added and well mixed by shaking. A considerable amount of heat is developed in the process. The flask is now fitted with a reflux condenser (Fig. 17) placed upon the water-bath and heated for 2–3 hours. The product contains, in addition to ethyl hydrogen sulphate, free sulphuric acid and unchanged alcohol. The liquid on cooling is poured into ½ litre of cold water in a large basin and well stirred. It is neutralised by adding chalk ground into a thin paste with water. This precipitates the free sulphuric acid as calcium sulphate and converts the ethyl hydrogen sulphate into the soluble

calcium salt. The mixture is heated, and filtered through a porcelain funnel with a filter-pump (Fig. 18), and the precipitate pressed well down and washed with a little water. The clear filtrate is heated on the water-bath, and a solution of potassium carbonate (about 50 grams) is added in small quantities until the liquid is slightly alkaline. To ensure complete precipitation a little of the clear liquid should be tested with a solution of potassium carbonate before proceeding.

The calcium salt is thereby converted into the soluble potassium salt, and calcium carbonate is precipitated. The latter is removed

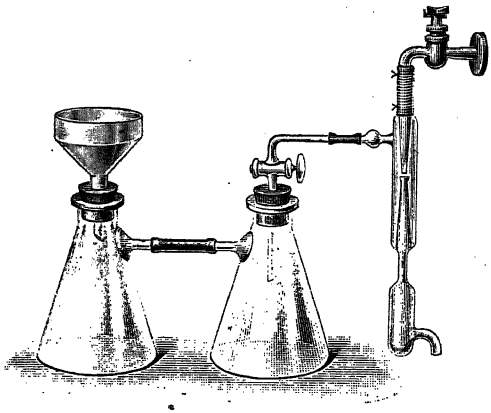


FIG. 18.

by filtration, as before, and the filtrate evaporated to dryness on the water-bath.

The following are the reactions involved :

1. $C_2H_6O + H_2SO_4 = \underset{\text{Ethyl hydrogen sulphate.}}{C_2H_5.H.SO_4} + H_2O.$

2. $2C_2H_5.H.SO_4 + CaCO_3 = \underset{\text{Calcium ethyl sulphate.}}{(C_2H_5SO_4)_2Ca} + H_2O + CO_2.$

3. $(C_2H_5SO_4)_2Ca + K_2CO_3 = \underset{\text{Potassium ethyl sulphate.}}{2C_2H_5.K.SO_4} + CaCO_3.$

The substance obtained in this way is not pure, for it may contain both potassium carbonate and possibly calcium sulphate, and must therefore be recrystallised from methylated spirit.

The following is the mode of procedure when a volatile or inflammable solvent is used : the substance is placed in a round flask attached to a reflux condenser and heated on the water-

bath. The form of apparatus is that already described in Fig. 17.

Small quantities of spirit are added and kept boiling until a solution is obtained. A small quantity of impurity may remain undissolved. The hot solution is at once decanted or filtered through a **fluted filter** (Fig. 19) or porcelain funnel (Fig. 13) and allowed to cool.

A **fluted filter** is made by first folding a large circular filter paper in the ordinary way. It is then half opened out and the two quadrants folded towards the middle line (Fig. 19*a*). This makes three creases with the hollows on the same side. The filter is now turned over and each section folded down the centre so that the hollows of the four new creases alternate with the

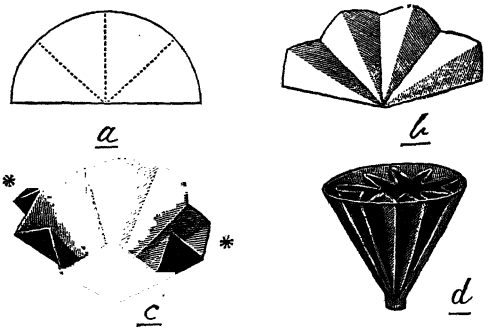


FIG. 19.

ridges of the three others as shown at *b*. The paper when opened now appears like *c*. The two rectangular flutings indicated by an asterisk have still to be divided by a crease down the middle. The filter is now pushed well into the funnel, the stem of which is cut off short as shown at *d*.

When the filtered liquid has stood for some time, and is quite cold, the crystalline deposit is separated by filtration and washed with a little cold spirit. It is dried on a plate of unglazed earthenware or on a thin pad consisting of three or four sheets of filter paper, with another sheet over the crystals to keep out the dust. On concentrating the mother liquors on the water-bath, a further quantity of crystals may be obtained.

The following reactions should be studied.

EXPT. 11.—Dissolve a little of the recrystallised salt in water and add barium chloride. There is no precipitate, as the barium

salt of ethyl hydrogen sulphate is soluble in water; but if the solution is boiled for a moment with a few drops of hydrochloric acid, a precipitate of barium sulphate will be formed.

This is another example of a **reversible reaction** (p. 29). The addition of hydrochloric acid liberates the free ethyl hydrogen sulphate, which is partly decomposed by the water into ethyl alcohol and sulphuric acid:

$$C_2H_5.H.SO_4 + H_2O = C_2H_6O + H_2SO_4.$$

That the action of sulphuric acid on alcohol is reversible is further shown by the fact that, if equal molecular proportions of the two constituents are taken, an equilibrium condition is established in which both free alcohol and free sulphuric acid are present, however long the mixture is heated:

$$C_2H_6O + H_2SO_4 \rightleftarrows C_2H_5.H.SO_4 + H_2O.$$

EXPT. 12.—**Preparation of Ethyl acetate** (Acetic ester).—A distilling flask ($\frac{1}{2}$ litre) is attached to a condenser and receiver. The flask is provided with a cork, through which a separating funnel is inserted, as in Fig. 16, p. 30. The mixture of 50 c.c. of concentrated sulphuric acid and 50 c.c. of absolute alcohol is poured into the flask, which is then heated in a bath of paraffin wax to 140°, and kept at this temperature. The mixture of equal volumes of acetic acid and alcohol is now added, drop by drop, from the tap-funnel at the speed at which the liquid distils, as in the preparation of ether (p. 39). When all the mixture has been added, the distillate, which contains the ester, and also acetic acid, alcohol, ether, and sulphurous acid, is shaken in a separating funnel with a strong solution of sodium carbonate (50 c.c.) until the upper layer of ethyl acetate ceases to redden blue litmus. The lower layer is removed as completely as possible, and a strong solution of calcium chloride (50 grams in 50 c.c. of water) added, and the shaking repeated. The lower layer of calcium chloride is run off, and the ethyl acetate carefully decanted from the mouth of the funnel into a dry distilling flask. A few pieces of solid calcium chloride are added, and, after standing over night, the ethyl acetate is distilled from the water-bath with a thermometer in the neck of the flask. The portion distilling below 74° contains ether, that boiling at 74°–79° is mainly ethyl acetate, and is separately collected.

$$C_2H_5(OH) + H_2SO_4 = C_2H_5.H.SO_4 + H_2O.$$
$$C_2H_5.HSO_4 + C_2H_4O_2 = C_2H_3O_2.C_2H_5 + H_2SO$$

Ethyl acetate is a colourless liquid which like most of the esters (*i.e.* the compounds of alcohols and organic acids) has a pleasant, fruity smell. It is specifically lighter than water and slightly soluble in, though not miscible with, water. If ethyl acetate is allowed to stand in contact with water, the water will after a time have a distinctly acid reaction. The acetate has been decomposed into alcohol and acetic acid—another example of reversibility:

$$C_2H_6O + C_2H_4O_2 \rightleftarrows C_2H_5.C_2H_3O_2 + H_2O.$$

Reversible or balanced actions.—In the several examples of balanced actions previously described we have seen that if one of the products of the reaction is removed, the equilibrium is disturbed, fresh quantities of the new substances are formed, and the reaction may ultimately reach completion.

In the case of ethyl acetate, the addition of sulphuric acid is required to remove the water. If the reverse process is the object in view, it is hastened by the removal of the acid, that is, by the addition of an alkali.

Thus, if we wish to break up ethyl acetate into acetic acid and alcohol, we boil it with a strong solution of caustic potash or soda:

$$C_2H_5.C_2H_3O_2 + H_2O\,[+\,KOH] = C_2H_6O + C_2H_4O_2\,[+\,KOH].$$

This process is called **hydrolysis**, and may be defined as a chemical change which is brought about by the addition of the elements of water. The particular kind of hydrolysis whereby an ester is decomposed into its constituents is sometimes termed **saponification**, as it is the essential process in soap making (p. 119).

EXPT. 13.—**Hydrolysis of Ethyl acetate.**—Heat 20 grams of ethyl acetate with three times its volume of aqueous potash solution of about 30 per cent. strength. The mixture is placed in a distilling flask, attached by the neck to an inverted condenser, and boiled over wire gauze. A piece of porous pot is placed in the flask to prevent bumping, and the side-tube of the distilling flask is temporarily closed with a stopper. When the layer of ethyl acetate has dissolved (the potassium acetate and ethyl alcohol being both soluble in water), the condenser is attached to the side-tube of the distilling flask and the liquid distilled. The alcohol

which passes over may be separated from the water by the addition of potassium carbonate; the latter causes the alcohol to float on the surface, and may then be withdrawn. The acetic acid remains in the distilling flask as the potassium salt. The alkali is carefully neutralised with sulphuric acid and the liquid evaporated to dryness. The dry residue is then distilled with strong sulphuric acid, when pure acetic acid passes over. The reaction is expressed by the following equation :—

$$\underset{\text{Ethyl acetate.}}{C_2H_5.C_2H_3O_2} + KOH = \underset{\text{Alcohol.}}{C_2H_6O} + \underset{\text{Potassium acetate.}}{C_2H_3O_2K}.$$

QUESTIONS ON CHAPTER II.

1. Describe the behaviour of ethyl alcohol with sodium, phosphorus chloride, hydrogen chloride and sulphuric acid. Point out any analogous reactions occurring between these reagents and water or caustic soda.

2. Give examples of the action of acids on ethyl alcohol. Explain why these reactions are usually incomplete.

3. What is meant by a *reversible reaction*? Why is sulphuric acid added to ethyl alcohol and acetic acid to form ethyl acetate, and caustic potash added to the latter to decompose it into its original constituents ?

4. Describe a method for preparing ethyl iodide. How would you ascertain its molecular formula ?

5. Describe the preparation of pure ethyl acetate. How would you obtain from it specimens of ethyl alcohol and acetic acid ? What weight of each is theoretically obtainable from 20 grams of ethyl acetate ?

6. Calculate the theoretical weight of bromine and hydrochloric acid, respectively, required to convert 10 grams of ethyl alcohol into ethyl bromide and ethyl chloride ; also the theoretical weights of the two products.

CHAPTER III

THE STRUCTURE OF ETHYL ALCOHOL AND ETHYL ETHER

We are now in a position to learn something about the structure of ethyl alcohol. If we consider the reactions just described we see that in one set the alcohol behaves like water and in another like a metallic hydroxide. We may tabulate them as follows:

Water.	*Ethyl alcohol.*
$H_2O+Na_2=2HONa+H_2$.	$2C_2H_6O+Na_2=2C_2H_5ONa+H_2$.
$H_2O+PCl_5=$ $HCl+HCl+POCl_3$.	$C_2H_6O+PCl_5=$ $C_2H_5Cl+HCl+POCl_3$.
$H_2O+PBr_3=3HBr+H_3PO_3$.	$3C_2H_6O+PBr_3=$ $3C_2H_5Br+H_3PO_3$.

In these reactions **ethyl**, C_2H_5, plays the part of an atom of hydrogen. Ethyl alcohol offers a further analogy with water forming **alcohol of crystallisation** with calcium chloride of the formula $CaCl_2 + 4C_2H_6O$.

The correspondence subsisting between the alcohols and the caustic alkalis is best observed in their behaviour with acids.

Caustic soda.	*Ethyl alcohol.*
$OH+HCl=NaCl+H_2O$.	$C_2H_6O+HCl=C_2H_5Cl+H_2O$.
$OH+HNO_3=NaNO_3+H_2O$.	$C_2H_6O+HNO_3=$ $C_2H_5NO_3+H_2O$.
$OH+H_2SO_4=$ $NaHSO_4+H_2O$.	$C_2H_6O+H_2SO_4=$ $C_2H_5.H.SO_4+H_2O$.
$OH+C_2H_4O_2=$ $NaC_2H_3O_2+H_2O$.	$C_2H_6O+C_2H_4O_2=$ $C_2H_5.C_2H_3O_2+H_2O$.

Here the ethyl group plays the part of sodium, and the compounds formed from the alcohol may be regarded as salts of ethyl. We may then build up the formula for ethyl alcohol

on the basis of that for water or caustic soda. In other word ethyl alcohol contains a **hydroxyl** (OH) group:

$$H—O—H \qquad Na—O—H \qquad C_2H_5—O—H$$

This hydroxyl group is characterised by the fact that b the action of phosphorus chloride it can be replaced by chlorin and by the further fact that the hydrogen of the group can b removed by metallic sodium.

The group C_2H_5, which preserves its integrity throughou the above series of compounds, is termed the **alcohol radica** a radical being a group of elements which behave like a singl atom, in this case hydrogen and sodium. Moreover, as it play the part of an atom of a univalent[1] element, it is called a univalen radical. There are many such univalent alcohol radicals, an they have received the general name of **alkyl** group or radical As caustic soda is also termed sodium hydroxide, so ethyl alcoho may be called **ethyl hydroxide.**

Before we can ascertain the arrangement of the atoms in th radical itself, we shall have to learn a number of new facts.

Supposing ethyl alcohol corresponds in structure with sodium hydroxide we may ask: Is there a compound which corresponds with sodium oxide, Na_2O, and sodium peroxide, Na_2O_2? The former, or diethyl oxide, $(C_2H_5)_2O$, is known, and is the familiar anæsthetic, **ether**; but the peroxide has not yet been obtained, though there is no apparent reason for its non-existence.

Ether.—Suppose we utilise the strong affinity which we know to exist between sodium on the one hand and iodine (also chlorine or bromine) on the other, and examine what happens when sodium ethoxide is brought into contact with ethyl iodide. A vigorous action occurs and a white salt (sodium iodide) is precipitated. The product is ethyl ether:

$$C_2H_5ONa + C_2H_5I = (C_2H_5)_2O + NaI.$$

EXPT. 14.—Dissolve 3 grams of sodium in 40 c.c. of pure alcohol contained in a flask attached to a reflux condenser. When the sodium has dissolved, add 15 grams of ethyl iodide and heat the mixture on the water-bath. In a few minutes a deposit of sodium iodide will be formed, and if the contents of the flask be distilled

[1] It is assumed that the significance of the term valency is understood.

on a water-bath, ether and alcohol will collect in the receiver, from which the ether may be separated by the addition of a saturated solution of common salt. The upper layer is then removed and dehydrated over solid calcium chloride, then decanted, and a few pieces of metallic sodium added.

It was by this method that Williamson, in 1851, was enabled to show that ether was diethyl oxide. But the common method for preparing the substance is much simpler.

The discovery of ether is attributed to Valerius Cordus in 1544. It was obtained by distilling pure spirits of wine with

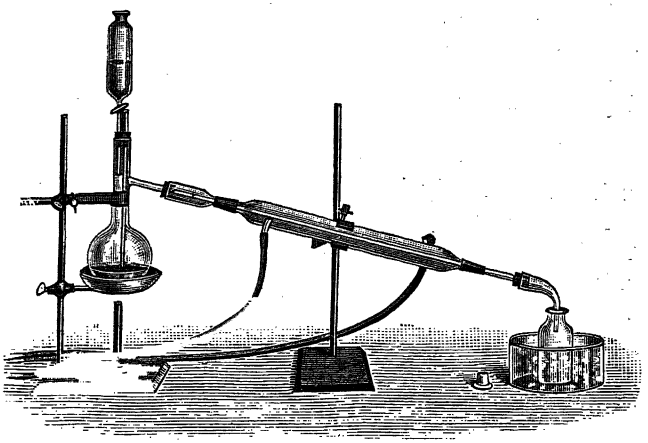


FIG. 20.

strong sulphuric acid. Boullay, early in the last century, found that the residue left in the retort, after removing the ether, was able to furnish a fresh supply by the addition of more alcohol. This discovery originated the modern method of manufacture, which is known as the **continuous ether process.**

EXPT. 15.—**Preparation of Ether.**—Fit up an apparatus like that in Fig. 20. It consists of a distilling flask ($\frac{1}{2}$ litre) furnished with a tap-funnel and thermometer, the bulb of which is immersed in the liquid in the flask. The liquid consists of a mixture of 80 c.c. of concentrated sulphuric acid, and 110 c.c. of absolute alcohol. The flask is heated on a sand-tray and kept at a temperature of 140°–145°, whilst fresh alcohol is allowed to drop slowly in

from the tap-funnel. Ether and water collect in the rece which is cooled in ice or cold water. The distillate is purifie shaking it with a little dilute caustic soda to remove sulphu acid, which is derived from a slight decomposition of the sulph acid. The caustic soda is drawn off, and a little strong solutio common salt added to dissolve out any alcohol which ma present. The salt solution is removed, and the ether first d drated over solid calcium chloride, and finally over met sodium, as described in Expt. 9, p. 30.

A small quantity of sulphuric acid can convert a very l amount of alcohol into ether. The explanation of this cur reaction was at one period a subject of much controversy. action of the sulphuric acid as a dehydrating agent, which was of the first and most obvious suggestions, was not long entertai seeing that both water and ether distil simultaneously—

$$\underset{\text{Ethyl alcohol.}}{2C_2H_6O} = \underset{\text{Ether.}}{C_4H_{10}O} + H_2O.$$

and it seemed highly improbable that the acid could rem water from the alcohol and part with it at the same temperatu

The following explanation was the one suggested by Williams and is now commonly accepted.

The first action of sulphuric acid on alcohol is to form et hydrogen sulphate and water. When fresh alcohol acts up the sulphate at 140°, ethyl ether is formed and sulphuric a is regenerated. The sulphuric acid, liberated in the seco stage of the process, is capable of transforming fresh alcol into ether. The sulphuric acid should thus be able to conv an infinitely large quantity of alcohol into ether. In practi this result is never attained, as some of the acid is decompos by carbonaceous by-products of the reaction. The equatio representing the reaction are as follows—

1. $C_2H_5.OH + H_2SO_4 = \underset{\text{Ethyl hydrogen sulphate.}}{C_2H_5.H.SO_4} + H_2O.$

2. $C_2H_5.HSO_4 + C_2H_5.OH = \underset{\text{Diethyl ether.}}{C_2H_5.O.C_2H_5} + H_2SO_4.$

Properties of Ethyl ether.—Ethyl ether is a very volati and exceedingly inflammable liquid. It should therefore be ke away from a flame. Its vapour is very heavy, and forms, wit air, an explosive mixture. It solidifies at $-117{\cdot}6°$.

EXPT. 16.—The density of ether vapour can be readily demonstrated by slightly tilting a beaker containing a little warm ether so that the vapour descends an inclined trough of cardboard. At the lower end a lighted burner is placed, and the vapour on reaching the burner is ignited, and the flame travels up the trough.

Ether, when inhaled, produces unconsciousness, and was introduced by Morton as an anæsthetic in 1846. It is also employed in the form of a spray, for producing local insensibility. The rapid evaporation of ether produces a low temperature, and this property is employed for refrigerating purposes.

EXPT. 17.—Pour a little ether into a beaker, and place it on a narrow board moistened with water. Blow a current of air through the ether by means of bellows for a few minutes. Hoar frost will form on the outside of the beaker, and the water below the beaker will freeze and fix it firmly to the board.

Ether is largely used as a solvent for resins, fats, oils, and alkaloids. It is frequently employed in the laboratory for extracting oils from water, especially when the oil is disseminated through the water in fine particles. When ether is shaken up with such a liquid, it dissolves the oily globules and unites them in a layer on the surface of the liquid. This layer is easily separated from the water by a tap-funnel, and when the ether has been distilled off, the oil remains.

That ethyl ether contains no replaceable hydrogen like alcohol is shown by the fact that when freed from alcohol and water it has no action on sodium. That it contains no hydroxyl group is further demonstrated by the absence of any action on phosphorus pentachloride.

EXPT. 18.—Add to a test-tube containing a small quantity of carefully purified ether a fragment of metallic sodium. There is little or no effervescence. The small amount of effervescence is usually due to absorption of moisture from the air. To a second test-tube add in the same way a few small pieces of phosphorus pentachloride. Here again there is no action.

Molecular formula of Ethyl ether.—That the molecular formula for ethyl ether is $C_4H_{10}O$ is readily determined by Victor Meyer's air displacement method already referred to (p. 16).

EXPT. 19.—**Vapour density of Ether.**—The method consists rapidly vaporising a known weight of a substance at a consta temperature at least 40°–50° above its boiling-point, in a spec form of apparatus which admits of the displaced air being collect and measured. The volur occupied by a given weig of the substance und known conditions is th ascertained, and from the data the density is calc lated. The following appar tus is required :—

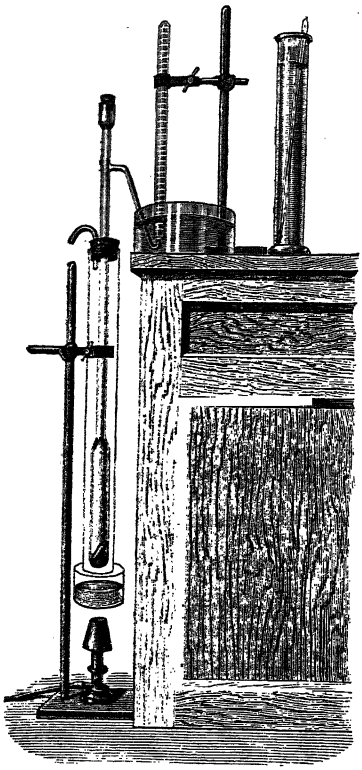


FIG. 21.—The Victor Meyer vapour density apparatus.

A Victor Meyer apparatu as shown in Fig. 21, co sists of an elongated gla bulb with a narrow sten and a capillary side-tub It is provided with a wel fitting rubber cork, whic can be pressed easily an tightly into the open end c the stem. The apparatu is clamped within an oute jacket of tin plate or copper which holds the boilin liquid required to produc a constant temperature It is represented as trans parent in Fig. 21.

Hofmann bottle.—The sub stance, if liquid, is intro duced into a small stoppered glass bottle known as Hofmann bottle (Fig. 22). The dry bottle with the stopper is carefully weighed and then filled with liquid through a tube drawn out into a wide capillary. The stopper is inserted and the bottle reweighed. It should hold about 0·1 gram of substance. The following apparatus is required: *a narrow graduated tube* holding 50 c.c. and



FIG. 22

divided into tenths of a c.c.; *a large crystallising dish* which serves as a gas trough; *a long and wide cylinder* in which the graduated tube can be submerged in water; *a Bunsen burner with chimney.*

The apparatus is set up as shown in Fig. 21. The Victor Meyer apparatus is thoroughly dried by blowing air through by means of a long glass tube which reaches to the bottom of the bulb. A small quantity of clean dry sand previously heated in a crucible, or a pad of asbestos is placed at the bottom of the bulb, to break the fall of the Hofmann bottle when it is dropped in. The bulb of the outer jacket is filled two-thirds full of water and the displacement apparatus is clamped within it, so that it nearly touches the liquid. The apparatus and jacket must be adjusted at such a height that the capillary side limb dips under the water contained in the crystallising dish placed on the bench. The graduated tube is filled with water and inverted under the water in the crystallising dish and clamped there until required. The burner, protected from draughts by the chimney, is lighted under the outer jacket and the displacement apparatus left open at the top. To avoid inconvenience arising from the steam, a split cork, into which a bent glass tube is inserted, is pushed loosely into the open end of the jacket.

Whilst the water is boiling steadily and not too violently, the substance is weighed in the Hofmann bottle. Before introducing the bottle and liquid the apparatus must be tested to ascertain if the temperature is constant. As a rule $\frac{1}{4}$ hour's boiling suffices. Push in the rubber cork and note if within the next minute or two any bubbles escape. If not, slip the graduated tube over the end of the side tube, and carefully remove the rubber cork so that no water enters the stem through the capillary. Remove the stopper of the Hofmann bottle before dropping it in, and at once push in the cork. Very shortly a stream of air bubbles will ascend the graduated tube. When, in the course of a minute or two, the bubbles cease, remove the cork from the apparatus and extinguish the burner. The graduated tube is transferred to the large cylinder of water by closing the open end with the thumb. Leave the tube in the water with the thermometer beside it for $\frac{1}{4}$ hour. Lift the graduated tube, and whilst holding it by a collar of paper adjust the levels inside and out. Read off the volume and note the temperature and barometric pressure.

The density is calculated as follows :—

If v is the volume, t the temperature, B the barometric pressure,

and f the vapour tension of water at $t°$, then the corrected volum is given by the formula

$$\frac{v \times (B - f) \times 273}{760 \times (273 + t)}.$$

This multiplied by 0·00009, the weight of 1 c.c. of hydrogen at o and 760 mm., gives the weight of hydrogen occupying the sam volume as the vaporised substance, from which the density $\Delta = \frac{W_s}{W_h}$ is obtained.

Example.—The following result was obtained with ether 0·1146 gram of ether gave 36·3 c.c. at 11° and 752 mm. f=10 mm at 11°.

$$\frac{36{\cdot}3 \times (752 - 10) \times 273 \times 0{\cdot}00009}{760 \times 284} = 0{\cdot}00306.$$

$$\frac{0{\cdot}1146}{0{\cdot}00306} = 37{\cdot}4.$$

Calculated for $C_4H_{10}O$: $\Delta = 37$.

If substances of higher boiling-point have to be vaporised, the water in the outer jacket is replaced by other liquids of correspondingly higher boiling-point.

The action of the metals and their compounds on Ethyl iodide (bromide or chloride).—We have studied two examples of these reactions, that of sodium hydroxide and sodium ethoxide on ethyl iodide (or chloride)—

$$C_2H_5I + NaOH = C_2H_5OH + NaI.$$
$$C_2H_5I + NaOC_2H_5 = (C_2H_5)_2O + NaI.$$

There are many other reactions of the same kind which are of the greatest importance. As they cannot be conveniently carried out in the laboratory without a considerable expenditure of time, the following equations should be carefully studied—

1. $C_2H_5I + KSH = \underset{\text{Ethyl mercaptan.}}{C_2H_5SH} + KI.$
2. $C_2H_5I + K_2S = \underset{\text{Ethyl sulphide.}}{(C_2H_5)_2S} + 2KI.$
3. $C_2H_5I + KCN = \underset{\text{Ethyl cyanide.}}{C_2H_5CN} + KI.$
4. $C_2H_5I + \underset{\text{Ammonia.}}{NH_3} = \underset{\text{Ethyl amine.}}{C_2H_5NH_2} + HI.$
5. $2C_2H_5I + \underset{\text{Silver sulphate.}}{Ag_2SO_4} = \underset{\text{Diethyl sulphate.}}{(C_2H_5)_2SO_4} + 2AgI.$
6. $C_2H_5I + \underset{\text{Silver acetate.}}{C_2H_3O_2Ag} = \underset{\text{Ethyl acetate.}}{C_2H_5.C_2H_3O_2} + AgI$

Supposing the halogen atom is completely removed by metallic sodium or other metal, then the radical, which cannot exist in the free state, joins itself to a second one, and a compound containing only carbon and hydrogen, or **hydrocarbon,** called **butane,** is formed, which belongs to the important class of **paraffins** (p. 81).

7. $2C_2H_5I + 2Na = \underset{\text{Butane.}}{C_4H_{10}} + 2NaI.$

Finally, supposing the iodine to be replaced by hydrogen, then another hydrocarbon, C_2H_6, or **ethane,** which is a gas, is produced. This also belongs to the same group of paraffins.

8. $C_2H_5I + H_2 = C_2H_6 + HI.$

EXPT. 20.—**Preparation of Ethane.**—Take a wide test-tube, furnish it with a well-fitting cork holding a tap-funnel and delivery tube. Remove the cork and introduce 5 grams of zinc dust; pour on 15 c.c. of a saturated solution of copper sulphate, stir well with a glass rod to prevent the particles caking together, and cool in cold water. Copper will be at once deposited on the zinc. Let the solid settle for a minute, decant the solution as far as possible, and pour on 10 c.c. of alcohol, shake well and decant, and repeat the process. Finally, pour on a further 5 c.c. of alcohol. Insert the cork with tap-funnel and delivery tube so that the latter dips under water, and drop in slowly from the tap-funnel 5 c.c. of ethyl iodide, shaking occasionally or warming gently until bubbles of gas begin to be evolved. Collect the gas in a test-tube over water. This is ethane, and when ignited burns with a non-luminous flame.

The hydrogen is supplied by the ethyl alcohol, and the reaction occurs according to the equation:

$$C_2H_5I + Zn + C_2H_5OH = Zn\begin{matrix} I \\ OC_2H_5 \end{matrix} + C_2H_6.$$

The copper forms an electrolytic couple with the zinc and accelerates the action.

QUESTIONS ON CHAPTER III

1. Why is the group C_2H_5 termed a *compound radical*?

2. How is ethyl iodide prepared? How does it react with (1) potassium hydroxide, (2) ammonia, (3) sodium?

3. What paraffins can be prepared from ethyl iodide ? Describ the reactions.

4. Ethyl ether may be described as *diethyl oxide*. Give you reasons for this statement.

5. Describe the preparation and purification of diethyl ether b the *continuous process*.

6. Discuss fully how the structure of ethyl ether has bee ascertained.

7. What is meant by the *hydroxyl group* ? Give your reason for the statement that ethyl alcohol contains this group.

CHAPTER IV

THE OXIDATION OF ETHYL ALCOHOL

Acetaldehyde.—Ethyl alcohol readily undergoes oxidation. If a red hot spiral of platinum is suspended near the surface of warm alcohol, the wire continues to glow and an acrid smell is soon apparent. This is the oxidation product, known as **acetaldehyde.**

$$C_2H_6O + O = \underset{\text{Acetaldehyde.}}{C_2H_4O} + H_2O$$

Oxidation takes place by means of the oxygen of the air, which is occluded, or absorbed, by the platinum, and is then in a much more active condition than free oxygen.

EXPT. 21.—Make a spiral of platinum wire by wrapping it round a glass rod, and leave one long end. Attach the long end to a short glass rod, which serves to suspend the spiral horizontally within a small beaker. Pour in ethyl alcohol until the surface of the liquid rises to about one-eighth of an inch from the spiral. Gently warm the alcohol. Remove the spiral, heat it red-hot, and replace it quickly. It will continue to glow, evolving acetaldehyde. The arrangement of the apparatus is shown in Fig. 23.

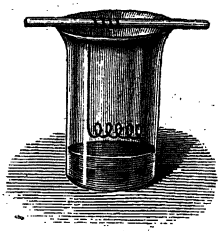


FIG. 23.

Alcohol may also be oxidised by oxidising agents in solution.

EXPT. 22.—Warm a solution of sodium dichromate, acidified with dilute sulphuric acid, with a few drops of alcohol. The solution soon becomes green from the reduction of the dichromate to chromic sulphate, and, at the same time, the peculiarly penetrating smell of acetaldehyde is evolved. The same result is

obtained with potassium permanganate solution. The permanganate is reduced to the brown peroxide of manganese on warming with the alcohol, and acetaldehyde is formed.

$$3C_2H_6O + Na_2Cr_2O_7 + 4H_2SO_4 = 3C_2H_4O + Cr_2(SO_4)_3 + Na_2SO_4 + 7H_2O.$$

$$3C_2H_6O + 2KMnO_4 = 3C_2H_4O + 2MnO_2 + 2KOH + 2H_2O.$$

The above experiment may be carried out on a larger scale.

EXPT. 23.—**Preparation of Acetaldehyde.**—A round flask (1½ litre) is provided with a well-fitting double bored cork. A bent

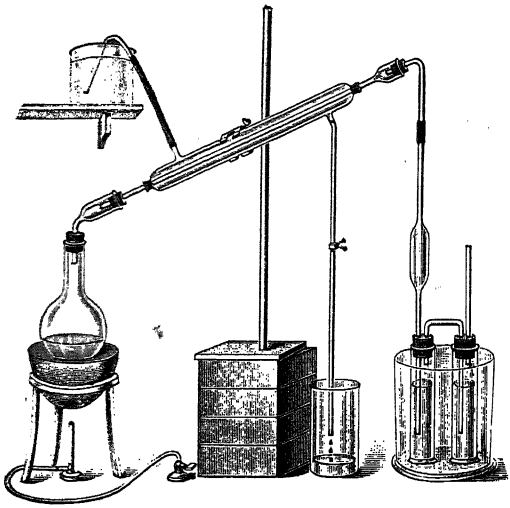


FIG. 24.

tube, which passes through one hole, connects the flask with a condenser and receiver. A tap-funnel is inserted through the other hole, as in Fig. 16, p. 30. The flask is placed upon a sand-bath, and the receiver is cooled in ice. It is important that all the corks should be tight, as a small leak will considerably diminish the yield. One hundred grams of sodium dichromate in small pieces and 400 c.c. of water are placed in the flask and gently warmed. The flame is then removed, and a mixture of 125 c.c. absolute alcohol and 75 c.c. concentrated sulphuric acid, which may be used warm, is slowly added from the tap-funnel. The flask is occasionally shaken. A considerable rise of temperature occurs and the liquid darkens, whilst aldehyde, with a little water and

alcohol, distils. When the mixture has all been added, the flask is heated on the sand-bath until all the aldehyde has distilled (about 150 c.c.). This may be determined by removing the cork from the flask and noticing if the smell of aldehyde is still perceptible.

Purification of Acetaldehyde.—To separate the aldehyde, it is converted with ammonia into the solid crystalline compound known as **aldehyde-ammonia,** which is insoluble in ether. The distillate is first purified by redistillation on the water-bath in the apparatus shown in Fig. 24.

The flask is attached to an upright condenser in which the water is kept at a temperature of 30°–35°. Alcohol and aqueous vapour condense in the condenser; the aldehyde, on the other hand, passes by a tube attached to a 100 c.c. pipette into two narrow (100 c.c.) cylinders, one-third filled with the dry ether, and cooled in ice-water. The aldehyde readily dissolves in the ether and is rapidly absorbed. If the ethereal solution is now saturated with dry ammonia gas, the whole of the aldehyde separates out in the form of colourless crystals of aldehyde-ammonia,

$$C_2H_4O + NH_3 = \underset{\text{Aldehyde-ammonia.}}{C_2H_4O.NH_3}.$$

The apparatus for preparing the dry ammonia is shown in Fig. 25. The flask containing strong ammonia solution is heated by a *small* flame, when the gas is readily evolved and passes up the tower, which is filled with soda-lime or quicklime. The ethereal solution is saturated with the gas, and is then allowed to stand for an hour.

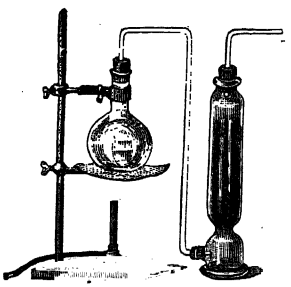


FIG. 25.

The ether is then decanted from the crystals, which are drained at the filter-pump, washed with a little ether, and finally dried in the air on filter-paper. The yield of aldehyde-ammonia is 25–30 grams. It may be used for the reactions described below.

Pure aldehyde may be prepared from the aldehyde-ammonia as follows: The crystals are dissolved in an equal weight of water, and distilled on the water-bath with a mixture of 1½ parts of concentrated sulphuric acid and 2 parts of water, the receiver being well cooled in ice. The temperature of the water-bath is gradually raised until the water begins to boil, and the distillation is then interrupted. The distillate is dehydrated over an equal bulk of

calcium chloride, from which it is distilled in the water-bath, heated to 30°. The anhydrous aldehyde is kept in a well-stoppered bottle.

$$2C_2H_4O.NH_3 + H_2SO_4 = C_2H_4O + (NH_4)_2SO_4.$$

Properties of Acetaldehyde.—Acetaldehyde is a colourless liquid, boiling at 21°. It is soluble in water and has a specific gravity of 0·807 at 0°. It possesses a strong reducing action.

When an alkaline solution of a copper salt, such as Fehling's solution, is warmed with an aldehyde, the cupric oxide, which is present in solution, is reduced to cuprous oxide, and acetic acid is formed at the same time :—

$$2CuO + C_2H_4O = Cu_2O + C_2H_4O_2.$$

EXPT. 24.—Add a few drops of acetaldehyde to Fehling's solution and boil. A red precipitate of cuprous oxide is formed. Fehling's solution for qualitative tests is prepared by dissolving 3 to 4 grams of copper sulphate together with 5 to 6 grams of Rochelle salt in 50 c.c. of water. This is mixed, when required for use, with about an equal volume of caustic soda solution of 10 per cent. strength, when a clear blue solution results. The Rochelle salt serves to keep the cupric oxide in solution when alkali is added.

A similar reaction occurs with an ammonical solution of silver nitrate. This solution may be regarded as containing dissolved silver oxide. When a few drops of aldehyde are added to it and the liquid warmed, a metallic mirror of silver is deposited and acetic acid is formed :—

$$Ag_2O + C_2H_4O = Ag + C_2H_4O_2.$$

EXPT. 25.—Add a few drops of acetaldehyde to half a test-tube of ammonia-silver nitrate solution, and place it in hot water. In a few minutes a mirror will cover the sides of the test-tube. The silver solution is prepared by adding dilute ammonia to silver nitrate until the precipitate of silver oxide just dissolves.

Acetaldehyde combines with a molecule of sodium bisulphite forming a crystalline compound, C_2H_4O, $NaHSO_3$.

A further reaction for aldehyde is known as **Schiff's test.** If a little aldehyde is added to magenta solution, which has been rendered nearly colourless with sulphur dioxide, a violet colour is produced.

EXPT. 26.—Make a dilute solution of magenta (fuchsine or rosaniline hydrochloride) in water, and bubble sulphur dioxide through it until the colour disappears. Add to the solution a few drops of aldehyde, and observe the violet coloration.

Acetaldehyde combines with hydroxylamine, NH_2OH, and also with phenylhydrazine, $C_6H_5NH.NH_2$, and other compounds containing the group NH_2. The former is called **acetaldoxime** and the latter **acetaldehyde-phenylhydrazone.**

$$C_2H_4O + H_2N.OH = \underset{\text{Acetaldoxime.}}{C_2H_4{:}NOH} + H_2O.$$

$$C_2H_4O + H_2N.NH.C_6H_5 = \underset{\text{Acetaldehyde-phenylhydrazone.}}{C_2H_4{:}N.NHC_6H_5} + H_2O.$$

EXPT. 27.—Add to a little phenylhydrazine rather more than an equal volume of glacial acetic acid and dilute the solution with two to three volumes of water. Add a little aldehyde. A turbid liquid results, which is due to the formation of the phenylhydrazone, an oily liquid insoluble in water. It may be extracted with ether by shaking and separating the ether with a tap-funnel. When the ether evaporates, aldehyde-phenylhydrazone remains.

Caustic alkalis differ from ammonia in their effect upon aldehydes. The lower members of the series are transformed by the caustic alkalis into brown, resinous bodies of unknown constitution.

EXPT. 28.—Boil a little acetaldehyde with caustic potash solution. The liquid soon becomes yellow, and eventually deposits a brown, resinous substance known as **aldehyde resin.**

Aldehyde combines with alcohol in presence of solid calcium chloride to form a liquid termed **acetal** which boils at 104°.

$$C_2H_4O + 2C_2H_6O = \underset{\text{Acetal.}}{C_2H_4(OC_2H_5)_2} + H_2O.$$

With concentrated sulphuric acid, aldehyde is converted into **paraldehyde,** a liquid which boils at 124° and is insoluble in water. It has the formula $(C_2H_4O)_3$, or three times the molecular weight of acetaldehyde, and is used in medicine as a hypnotic.

EXPT. 29.—Add a drop or two of concentrated sulphuric acid to a few c.c. of acetaldehyde. The mixture boils up suddenly, and on adding water the paraldehyde separates as an oil.

If the same reaction is carried out at 0°, **metaldehyde,** a colourless solid $(C_2H_4O)_3$, isomeric, therefore, with paraldehyde, is formed.

We may add to the above the fact that if phosphorus pen chloride is added to pure acetaldehyde cooled in ice, the pen chloride rapidly dissolves without the evolution of hydro chloride, and **ethylidene chloride** is formed.

$$C_2H_4O + PCl_5 = \underset{\text{Ethylidene chloride.}}{C_2H_4Cl_2} + POCl_3.$$

Additive compounds.—If hydrogen cyanide is added acetaldehyde the compound, $C_2H_4O.HCN$, known as **acetal hyde-cyanhydrin** is formed.

$$C_2H_4O + HCN = \underset{\text{Aldehyde-cyanhydrin.}}{C_2H_4O.HCN}.$$

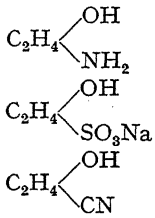
Such a compound is called an **additive** or **addition compou** Aldehyde-sodium bisulphite and aldehyde-ammonia are a examples of additive compounds (pp. 49, 50).

Structure of Acetaldehyde.—We are now in a position ascertain something about the structure of acetaldehyde. If look through the above series of reactions we shall see that t oxygen atom is differently combined from that in ethyl alcoh since it possesses totally different properties. By the action phosphorus pentachloride it is replaceable by two atoms chlorine, whereas in alcohol both hydrogen and oxygen w removed together, and replaced by one atom of chlorine, hydrog chloride being evolved (p. 28). Then again the oxygen is remov in the form of water, by union with alcohol (p. 51) and phenyll drazine (Expt. 27). Furthermore, the aldehyde forms a ser of additive compounds with ammonia, sodium bisulphite a hydrogen cyanide.

The behaviour of the compound finds a ready explanation the supposition that the oxygen atom is unsaturated, which impl first, that it is loosely attached, and, secondly, that it satura itself by forming additive compounds. For the present we v indicate the attachment by the formula, $C_2H_4:O$. We cann penetrate beyond this point until we know something more abo the arrangement of the carbon and hydrogen atoms in the mainder of the molecule.

The additive compounds are usually represented by formu

on the assumption that the oxygen being a negative element seizes on the electropositive hydrogen thus :—



Aldehyde-ammonia.

Aldehyde-sodium bisulphite.

Aldehyde-cyanhydrin.

Isomerism, polymerisation, and condensation.—In Expt. 29 of the foregoing series it was pointed out that two different substances having the same formula were obtained by the action of concentrated sulphuric acid at different temperatures on acetaldehyde—the one a liquid, paraldehyde, and the other a solid, metaldehyde. This is a case of **isomerism,** that is to say, of the existence of two distinct individuals having the same molecular weight but possessing different properties. The difference is undoubtedly due to a different arrangement of their atoms. Another point of interest is their method of formation. No elements are removed from the aldehyde in the process, but in each case the molecular weight is trebled. Both compounds, moreover, may be reconverted by distillation with dilute sulphuric acid into the original acetaldehyde. The phenomenon is termed **polymerisation,** and may be defined as a change produced by the union of the molecules of a compound to form a new substance having a multiple of the original molecular weight, and which may be easily converted into the original substance. Acetaldehyde, when allowed to remain for some time in contact with hydrochloric acid or a solution of potassium carbonate, undergoes a change of a somewhat similar character, inasmuch as the product called **aldol** has the double molecular weight

$$2C_2H_4O = \underset{\text{Aldol.}}{C_4H_8O_2}.$$

but the substance cannot be resolved by any simple reaction into its original constituents. The union of the two molecules is a much firmer one, and hence this process is distinguished from the former by the term **condensation.** When we have a fuller

knowledge of the structure of acetaldehyde we shall be able offer an explanation of the difference between the structure the polymerised and condensed products. For the present it mu remain unexplained.

Acetic acid.—If ethyl alcohol and acetaldehyde are furth oxidised they are converted into acetic acid by the addition to t latter of one atom of oxygen.

$$\underset{\text{Ethyl alcohol.}}{C_2H_6O} \rightarrow \underset{\text{Acet-aldehyde.}}{C_2H_4O} \rightarrow \underset{\text{Acetic acid.}}{C_2H_4O_2}$$

The oxidation may be effected in a very simple manner b passing the vapour of alcohol mixed with air over platinise asbestos (p. 71).

EXPT. 30.—Fill a tube about a foot long with platinised asbesto The asbestos is prepared by soaking it in platinic chloride, an then heating it until it turns black. A wash-bottle, containin ethyl alcohol, is attached to one end of the tube, which is fixe horizontally. The alcohol is gently warmed, and a rapid currer of air bubbled through the alcohol, and then over the asbesto The asbestos glows, and aldehyde and acetic acid are formed, th latter being readily indicated by holding a piece of moistened blu litmus paper at the open end of the tube, when the paper soo turns red.

Acetic acid is usually prepared either from pyroligneous aci obtained in the distillation of wood or as vinegar by the **acetou fermentation** of alcoholic liquids.

EXPT. 31.—To illustrate the first process, introduce into a har glass tube some small pieces of hard wood or sawdust, and attache to a receiver and delivery tube as shown in Fig. 26. Heat the tub gently at first and then more strongly. A watery liquid and som tar collect in the receiver, and inflammable gas is given off. Tes the aqueous portion with blue litmus paper. It will be found t have an acid reaction. The acid is acetic acid. But there ar other constituents of the aqueous distillate consisting mainly o two important ingredients of which we shall learn more presently namely, **wood spirit** or **methyl alcohol**, and **acetone.**

On the industrial scale the process is conducted in iron retorts and the aqueous distillate, or **pyroligneous acid**, is withdrawn fron the tar, which is known as **wood-tar.** This pyroligneous acid

which contains about 10 per cent. of acetic acid, 1–2 per cent. of methyl alcohol, and about 0·1–0·5 per cent. of acetone, is neutralised with lime, and the methyl alcohol and acetone are distilled off. The solution of the lime salt is evaporated, tarry and resinous matters being removed from the surface. The dry calcium acetate is gently heated to carbonise some of the impurities, and is then known as "grey acetate." It is distilled in copper vessels with strong hydrochloric acid sufficient to decompose the salt :—

$$\underset{\text{Calcium acetate.}}{(CH_3.CO_2)_2Ca} + 2HCl = \underset{\text{Acetic acid.}}{2CH_3.CO_2H} + CaCl_2$$

The distillate, which contains about 50 per cent. of acetic acid, is further purified by a second distillation over a little potassium

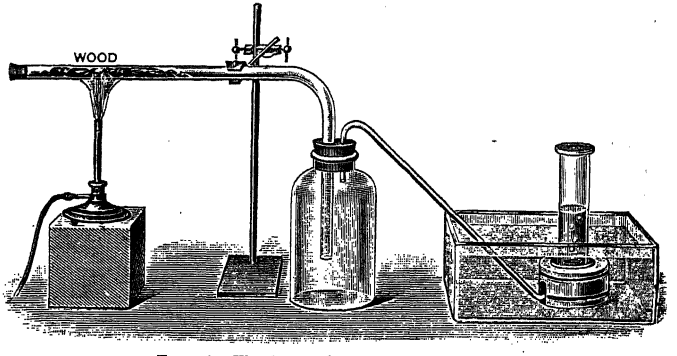


FIG. 26.—The destructive distillation of wood.

dichromate. **Glacial acetic acid** is obtained by first converting the acid into the sodium salt by neutralising with soda. The sodium salt, $C_2H_3O_2Na + 3H_2O$, is then fused to expel the water of crystallisation, and then distilled with concentrated sulphuric acid. The pure acid solidifies on cooling, and forms a colourless, crystalline mass, from which the name **glacial** has originated. It melts at 16·7°, boils at 119°, and has a specific gravity of 1·052 at 16·5°.

EXPT. 32.—**Preparation of pure Acetic acid.**—Place in a distilling flask attached to an ordinary condenser and receiver 30 grams of anhydrous sodium acetate and add slowly 15 c.c. of conc. sulphuric

acid and distil. Pure or glacial acetic acid distils and freezes to a transparent solid if cooled in ice. The anhydrous sodium acetate is prepared by fusing in a clean iron (sand) tray 50 grams of the crystallised acetate until it melts in its water of crystallisation, then becomes solid and finally at a higher temperature fuses to a transparent liquid. The acetate must be continually stirred or it will char.

Vinegar.—The souring of wine and beer when exposed to the air, from which the name acetic (*acetus*=vinegar) is derived, is due to the vinegar organism, mother of vinegar, or acetous ferment (*Mycoderma aceti*). It consists of cells constricted in the middle and often united in a chain (Fig. 27). The activity of the organism is prevented by strongly alcoholic liquids, such as spirits, port and sherry, and wines containing more than 15 per cent. of alcohol, which consequently do not turn sour. The methods used in the manufacture of vinegar are essentially alike. An alcoholic liquid, containing not more than 10 per cent. of alcohol, is added to vinegar from a previous operation, containing the organism, and the liquid is freely exposed to the air. The organism acts as a carrier of oxygen between the air and the alcohol. In the manufacture of **malt vinegar**, the fermented wort, produced in the same manner as whisky, is poured into casks containing vinegar. The casks are aerated by leaving the bung-hole open and perforating the ends near the top. When the transformation is complete a portion of the vinegar is withdrawn and the casks refilled with fresh liquor. **Wine vinegar** is made in the wine-growing districts of the Continent, and is produced from the poorer qualities of wine, in much the same manner as malt vinegar. It contains 6–8 per cent. of acetic acid, and owes its aroma to ethyl acetate and other substances present in the wine.



FIG. 27.—Vinegar organism (*Mycoderma aceti*). Same magnification as yeast (p. 22).

Quick Vinegar process.—The vinegar generator or "graduator" is a large cask with two perforated partitions of wood placed a little distance from the top and bottom. Short threads are suspended through the holes in the top partition.

To provide for the circulation of air, holes are bored in the sides of the cask above the lower partition. Birch twigs are packed in between the two partitions (Fig. 28). The twigs are first covered with the mother of vinegar by pouring on strong vinegar. Weak spirit containing 5–7 per cent. of alcohol is slowly run in from the top and trickles over the twigs, in the course of which the alcohol is converted into vinegar. The liquor runs out below, and having passed through a second time is finally clarified by running it over beech-wood shavings. The operation is conducted so that a constant temperature of 35° is maintained within the cask. If too little air is admitted, acetaldehyde is formed. If oxidation becomes too active or too prolonged, the alcohol is oxidised to carbon dioxide and water.

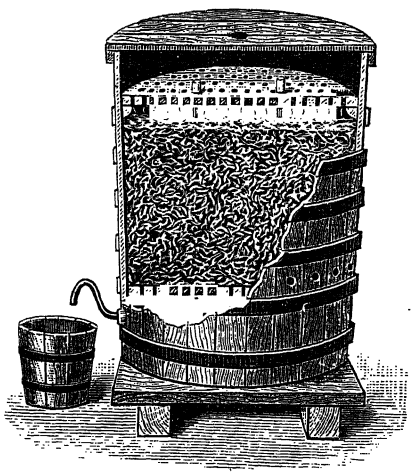


FIG. 28.—Quick vinegar process.

Vinegar is never used in the preparation of pure acetic acid, which is entirely derived from pyroligneous acid, as described above.

Properties of Acetic acid.—Pure acetic acid is a useful solvent for organic substances. As it is little affected by oxidising agents, it is frequently used as a solvent for chromium trioxide, where a powerful oxidising agent is required. The addition of water to acetic acid produces contraction in volume, so that an aqueous solution may have a higher specific gravity than the pure acid.

Tests for Acetic acid.—The volatility of acetic acid renders its detection a comparatively simple matter. The liquid to be tested is distilled, and the acid distillate neutralised with soda and evaporated to dryness. On the addition of concentrated sulphuric acid, the strong smell of vinegar is at once apparent,

or if a little alcohol is added before the addition of the sulphu acid, the fragrant smell of ethyl acetate is observed (p. 34).

$$CH_3.CO.OH + C_2H_5OH = CH_3.CO.OC_2H_5 + H_2O$$

Ethyl acetate.

Acetic acid is also detected by the red coloration which t solution of a neutral salt gives with ferric chloride. The r solution of ferric acetate loses acetic acid on boiling, and forr an insoluble basic salt.

The Acetates.—Most of the normal salts of acetic acid a soluble in water. Lead acetate, or **sugar of lead,** $Pb(C_2H_3O$ $+ 3H_2O$, is obtained by dissolving lead carbonate in acetic aci A solution of the normal salt dissolves lead oxide and forr **basic acetate of lead.**

Acetic acid is used in the manufacture of white lead, by exposir sheets of metallic lead to the combined action of acetic acid ar carbon dioxide. **Verdigris,** or basic acetate of copper, $(C_2H_3O_2)_2($ $+ Cu(OH)_2$, is used as a pigment, and is obtained by placir cloths dipped in vinegar in contact with sheets of copper. E contact with the air, a crust of the basic acetate is formed on th surface of the copper, and is scraped off and ground up.

Schweinfurt green, $(C_2H_3O_2)_2Cu + (AsO_3)_2Cu_3$, is obtaine by precipitating a solution of copper acetate with sodium arsenit and is used as a pigment. **Iron liquor** and **red liquor** are solution of the acetates of iron and aluminium, and used as **mordants** i calico printing and dyeing.

When the acetates, with which the cotton is impregnated, ar heated, acetic acid is driven off, and the aluminium and ferri oxides remain firmly attached to the fibre, and fix the colourin matter with which the cloth is printed, or dyed. A substanc which serves to attach colouring matter to cloth is termed **mordant** (*mordre*, to bite).

Iron liquor is prepared by dissolving scrap iron in commercia acetic acid; red liquor is obtained by precipitating a solution o lead acetate with aluminium sulphate and filtering off the lead sulphate.

Molecular formula for Acetic acid.—The fact that aceti acid forms only one series of salts (unlike sulphuric or phosphori acid, which form both acid and neutral salts) indicates that it is a

monobasic acid. Its molecular formula may therefore be determined from one of its neutral salts by ascertaining the weight of metal contained in a given weight of the salt. The weight of metal, if univalent, must bear to the weight of salt the ratio of one atom of metal to the molecular weight of the salt.

EXPT. 33.—**Molecular weight of Acetic acid.**—Dissolve 2 grams of silver nitrate and an equal weight of crystallised sodium acetate, separately, in 20 c.c. of water, cool and mix the two solutions. Shake well, filter at the pump, and wash free from sodium nitrate with cold water. Press well down and dry the precipitate in a vacuum desiccator over sulphuric acid in the dark. When quite dry weigh out carefully about 0·5 gram into a weighed porcelain crucible, cover with the lid and heat cautiously at first and then strongly until the weight is constant. The silver salt is decomposed and leaves a dull white residue of silver. If W is the weight of salt, w the weight of silver, the molecular weight of the silver salt is determined by the following formula :—

$$\frac{W \times 108}{w}$$

By deducting 108 for the atom of silver and adding 1 for the hydrogen which replaces the metal in the acid, the molecular weight of the acid is given.

Example.—0·475 gram of silver acetate gave on heating 0·305 gram of silver.

$$\text{M. W. of acetic acid} = \frac{0{\cdot}475 \times 108}{0{\cdot}306} - 107 = 60{\cdot}6.$$

M. W. calculated for $C_2H_4O_2 = 60$.

Structure of Acetic acid.—Before it is possible to determine the structure of acetic acid further properties of the acid will have to be examined.

EXPT. 34.—Add a fragment of metallic sodium to a little acetic acid ; effervescence occurs and the sodium passes into solution. When dissolved, evaporate to dryness on the water-bath ; sodium acetate is left.

$$C_2H_4O_2 + Na = C_2H_3O_2Na + H.$$

EXPT. 35.—Add to a small quantity of pure acetic acid in a test-tube a little phosphorus pentachloride. A vigorous action sets in and fumes of hydrogen chloride are evolved.

$$C_2H_4O_2 + PCl_5 = C_2H_3OCl + POCl_3 + HCl.$$

The product of the last reaction is **acetyl chloride.** It is more conveniently prepared by the method described on p. 62.

Comparing these two reactions with the very similar behaviour of ethyl alcohol (pp. 27, 28) it is clear that we are dealing with a compound containing a hydroxyl group. The formula may therefore be written $C_2H_3O.OH$. If sodium or potassium acetate is heated with caustic soda or soda-lime, the acetate is broken up into the hydrocarbon, **marsh-gas** or **methane**, CH_4, and sodium carbonate.

$$C_2H_3O_2Na + NaOH = CH_4 + Na_2CO_3.$$

EXPT. 36.—**Preparation of Methane.**—Powdered potassium acetate (20–30 grams) is mixed with three times its weight of soda-

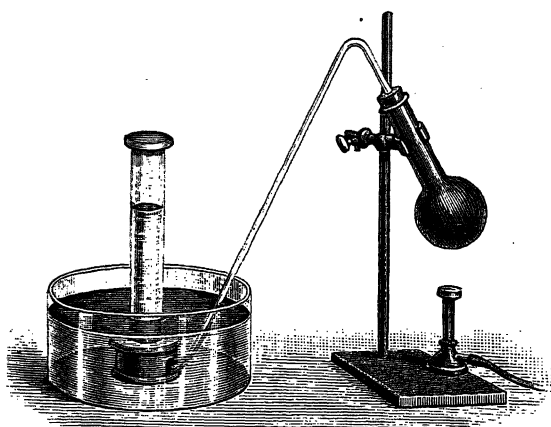


FIG. 29.—Preparation of marsh-gas from potassium acetate.

lime. The mixture is introduced into a glass or copper flask which is inclined as in Fig. 29. The flask is closed with a cork, into which a delivery-tube is inserted. The flask is strongly heated, and after the air has been expelled the gas is collected in a gas bottle over water, and the bottle, when full, is closed with a stopper. The gas is very far from pure, and burns with a luminous flame. To remove the luminous hydrocarbons the vaselined stopper is raised slightly and a little concentrated sulphuric acid is poured in quickly and rinsed round, and the bottle is quickly closed and left for a few hours. The gas then burns with a non-luminous flame.

Other ways of preparing this gas are mentioned later (p. 92).

It is clear from this reaction that the two carbon atoms in acetic acid have been severed and it is further evident that, in acetic acid, one is loaded with hydrogen and the other with oxygen. Assuming for the moment that one carbon atom carries the three hydrogen atoms and that the other carbon atom, the hydroxyl group and the remaining oxygen atom, the formula for acetic acid will appear thus :—

$(CH_3)CO_2H$

Acetic acid.

QUESTIONS ON CHAPTER IV.

1. Describe the preparation of pure acetaldehyde and give its characteristic reactions.

2. What is meant by the terms **polymerisation** and **condensation**? Give examples.

3. Give a list with formulæ of the **additive compounds** of acetaldehyde.

4. Describe a method for separating the constituents of a mixture containing methyl alcohol and acetic acid.

5. Discuss the structure of acetic acid.

6. How would you propose to obtain a specimen of pure acetic acid from vinegar?

7. Describe the "quick vinegar" process.

8. The ratio of carbon, hydrogen and oxygen in acetic acid can be expressed by the formula CH_2O. What are the reasons that have led to the formulæ $C_2H_4O_2$ and $CH_3.CO.OH$ being used instead?

9. You are given the product of the distillation of wood. Describe how a specimen of pure acetic acid could be obtained from it.

10. What would be the difference in the percentage of silver in silver acetate supposing the latter were a dibasic instead of a monobasic acid?

11. Give your reasons for writing $C_2H_4{:}O$ as the formula for acetaldehyde.

12. Twenty-five c.c. of dilute acetic acid neutralise 20 c.c. of a solution of caustic soda containing 40 grams per litre. Calculate the strength in grams per litre of the acid.

CHAPTER V

SOME DERIVATIVES OF ACETIC ACID

Acetyl chloride.—As already stated phosphorus chloride converts acetic acid into acetyl chloride. With phosphorus trichloride the following reaction occurs :—

$$3C_2H_4O_2 + PCl_3 = \underset{\text{Acetyl chloride.}}{3CH_3.COCl} + 3HCl + H_3PO_3.$$

EXPT. 37.—**Preparation of Acetyl chloride.**—A distilling flask, through the neck of which a tap-funnel is inserted, is attached to a condenser and receiver. The receiver should be connected with a tower of soda-lime, to absorb the hydrochloric acid evolved (see Fig. 16, p. 30) ; otherwise, the operation must be conducted in a fume-cupboard. Fifty grams of glacial acetic acid are placed in the flask, and 40 grams of phosphorus trichloride slowly added from the tap-funnel. The flask is gently warmed in the water-bath to 40°–50°, until the evolution of hydrochloric acid gas slackens. The water-bath is then heated to boiling, when the acetyl chloride distils. It boils at 55°.

Acetyl chloride may be regarded as composed of the radical C_2H_3O, called the *acetyl radical*, united to chlorine just as ethyl chloride consists of the radical, ethyl, united to chlorine. The general term for acid radicals is **acyl** in the same way that the alcohol radicals are called **alkyl**, and, like the latter, are mere names and have no separate existence. The structure of acetyl chloride is that of a substitution product of acetaldehyde, into which it may be transformed on reduction with sodium amalgam, and has therefore the formula :

$$\underset{\text{Acetyl chloride.}}{(CH_3)COCl}$$

Properties of Acetyl chloride.—Acetyl chloride is a colourless liquid with boiling-point lying between that of the corresponding aldehyde and acid. It fumes in moist air, and is very quickly decomposed by water. Hydrochloric acid is thereby evolved, and the original acid regenerated. Acetyl chloride, when acted on by water, gives acetic acid :

$$CH_3.CO\boxed{Cl + H}OH = \underset{\text{Acetic acid.}}{CH_3.CO.OH} + HCl.$$

EXPT. 38.—Add a few drops of water to a few drops of acetyl chloride in a test-tube. Decomposition takes place rapidly and the liquid becomes hot and boils, evolving hydrogen chloride.

The action of alcohol on the acid chloride is very similar to that of water. The alkyl salt, or ester, is formed and hydrochloric acid is evolved. Acetyl chloride and ethyl alcohol in this way give ethyl acetate :

$$CH_3.CO\boxed{Cl + H}OC_2H_5 = \underset{\text{Ethyl acetate.}}{CH_3.CO.OC_2H_5} + HCl.$$

This reaction is of great importance as a means of detecting the presence of a hydroxyl group in organic substances, and is more convenient than that requiring the use of sodium or of phosphorus pentachloride (pp. 27, 28), as the acetyl derivatives which are formed are usually easy to purify. Acetyl chloride, being readily obtainable, is convenient to employ. In compounds in which the hydroxyl group occurs, the hydrogen is replaced by **acetyl**, and forms an **acetoxyl group** :

$$-OH + CH_3.COCl = \underset{\text{Acetoxyl.}}{-O.CO.CH_3} + HCl.$$

EXPT. 39.—To about 1 c.c. of ethyl alcohol in a test-tube add, drop by drop, 1 c.c. of acetyl chloride and cool well under the tap. Then add about 1 c.c. of a solution of common salt, in which ethyl acetate is only slightly soluble. Ethyl acetate separates on the surface of the liquid and may be recognised by its fragrant smell.

Ammonia and ammonium carbonate react with acetyl chloride forming acetamide and ammonium chloride. This reaction is discussed more fully later (p. 197) :

$$CH_3.CO\boxed{Cl + H}\underset{\text{Ammonia.}}{NH_2} + NH_3 = \underset{\text{Acetamide.}}{CH_3.CO.NH_2} + NH_4Cl.$$

EXPT. 40.—If ammonia solution is added to acetyl chloride, he is evolved; but the acetamide, being very soluble in water, do not separate. If, however, a substituted ammonia, or amine (s p. 262) like phenylamine (aniline), $NH_2.C_6H_5$, be taken, the sol phenyl acetamide (acetanilide), $CH_3.CO.NHC_6H_5$, separates ou The experiment may be performed with a drop or two of ea substance.

Acetic anhydride is obtained by the action of the ac chloride on the sodium salt of the acid. Acetyl chloride and sodiu acetate yield acetic anhydride:

$$CH_3.CO.Cl + NaO.CO.CH_3 = \underset{\text{Acetic anhydride.}}{CH_3.CO.O.CO.CH_3} + NaCl.$$

The reaction is similar to that by which ethers are prepar (p. 38), and as the ethers are also named alkyl oxides, the compounds may be regarded as **acyl oxides**. By taking th chloride of one acid and the sodium salt of another, **mixe anhydrides** are formed, a process which resembles the metho of preparing mixed ethers (p. 110):

$$\underset{\text{Alkyl oxide.}}{(C_2H_5)_2O} \qquad \underset{\text{Acyl oxide.}}{(C_2H_3O)_2O}.$$

EXPT. 41.—**Preparation of Acetic anhydride.**—A retort, throug the tubulure of which a tap-funnel is fixed, is attached to a co denser and receiver. Fifty-five grams of fused sodium acetate ar placed in the retort, and 40 grams of acetyl chloride slowly ru in from the tap-funnel, the retort being cooled in water. Whe the acetyl chloride has been added, the contents of the retort ar well stirred with a glass rod and then distilled. Acetic anhydrid distils at 130°–140°.

The anhydride possesses a pungent smell, but does not fum It has a higher boiling-point than the acid from which it is derive In chemical behaviour it closely resembles the acid chlorid being decomposed by water, alcohol, and ammonia, but muc less rapidly than the acid chloride. Acetic anhydride yields th same products as acetyl chloride with these three reagents:

$$\underset{\text{Acetic anhydride.}}{(C_2H_3O)_2O} + H_2O = \underset{\text{Acetic acid.}}{2C_2H_4O_2}$$

$$(C_2H_3O)_2O + \underset{\text{Alcohol.}}{C_2H_5OH} = \underset{\text{Ethyl acetate.}}{CH_3.CO.OC_2H_5} + C_2H_4O_2.$$

$$(C_2H_3O)_2O + \underset{\text{Ammonia.}}{2NH_3} = \underset{\text{Acetamide.}}{CH_3.CO.NH_2} + \underset{\text{Ammonium acetate.}}{CH_3.CO.ONH_4}.$$

Action of Halogens.—Chlorine gas produces substitution in the CH_3 group, but has no action on the CO.OH group. Acetic acid forms chloracetic acid :

$$CH_3.CO.OH + Cl_2 = CH_2Cl.CO.OH + HCl.$$
Chloracetic acid.

and if the action is prolonged di- and tri-chloracetic acid are formed :

$CHCl_2.CO_2H$ Dichloracetic acid. $CCl_3.CO_2H$ Trichloracetic acid.

The action of chlorine is accelerated by sunlight, or by the presence of a carrier such as red phosphorus, sulphur, or iodine. Bromine acts like chlorine, but iodine is without direct action. The action of the halogens on the hydrocarbon radicals of the acids is therefore analogous to their behaviour with the paraffins (p. 90).

EXPT. 42.—**Preparation of Chloracetic acid.**—A round flask (25·0 c.c.) is fitted with a cork perforated with two holes ; through one a short condenser is attached and through the other a delivery tube passes to the bottom of the flask. Into the flask pour 100 c.c. of glacial acetic acid and add 10 grams of red phosphorus and weigh roughly. The flask is fixed on a water-bath. Dry chlorine, prepared by dropping concentrated hydrochloric acid on potassium permanganate and passing the gas through concentrated sulphuric acid, is bubbled in a rapid stream through the acetic acid, which is heated on the water-bath. Sunlight greatly assists the absorption of the gas, which is otherwise a very slow operation. When the flask has gained about 50 grams in weight the liquid in the flask is distilled over wire gauze and the portion boiling at 170°–190° collected. Chloracetic acid is a solid which melts at 63° and boils at 185°–187°.

EXPT. 43.—**Test for Halogens.**—Heat a fragment of copper oxide, held in the loop of a platinum wire, in the outer mantle of the non-luminous flame, until it ceases to colour the flame green. Let it cool a little, and then dust on some chloracetic acid or other halogen compound. Now heat again. A bright green flame accompanied by a blue zone immediately round the oxide indicates the presence of a halogen.

Like the alkyl halides (p. 44), the monohalogen derivatives of the acids exchange the halogen for other groups when acted

upon with various reagents. Monochloracetic acid, for example gives rise to the following products by the action of water, ammonia, and potassium cyanide respectively :

1. $CH_2Cl.CO_2H + H_2O = \underset{\text{Hydroxyacetic acid.}}{CH_2(OH).CO_2H} + HCl.$
2. $CH_2Cl.CO_2H + 2NH_3 = \underset{\text{Aminoacetic acid.}}{CH_2(NH_2).CO_2H} + NH_4Cl.$
3. $CH_2Cl.CO_2H + KCN = \underset{\text{Cyanacetic acid.}}{CH_2(CN).CO_2H} + KCl$

Acetone.—This substance has already been referred to as occurring with methyl alcohol in the aqueous distillate from wood (p. 54). It may also be obtained by the dry distillation of calcium acetate :

$$\underset{\text{Calcium acetate.}}{(C_2H_3O_2)_2Ca} = \underset{\text{Acetone.}}{C_3H_6O} + \underset{\text{Calcium carbonate.}}{CaCO_3}.$$

EXPT. 44.—**Preparation of Acetone.**—Distil 30 grams of dry calcium acetate in a retort, attached to a condenser and receiver. The retort must first be warmed and then strongly heated. A light brown liquid collects in the receiver. The liquid consists of acetone mixed with other products. By adding a few c.c. of a saturated solution of sodium bisulphite, a crystalline substance deposits on standing, which is a compound of acetone with sodium bisulphite. The acetone may be separated by distilling with sodium carbonate, but the quantity is usually too small for this purpose.

Acetone is now produced in considerable quantities by the action of a peculiar ferment on starch, and is largely used as a solvent, for the production of chloroform (p. 102), iodoform (p. 103), and in the manufacture of cordite (p. 166). It is a colourless liquid with a fragrant smell, mixes with water and boils at 56°. Its presence may be detected by the iodoform test (p. 25) which is the same as for ethyl alcohol. This reaction also serves for its quantitative estimation.

The properties of acetone resemble in many respects those of acetaldehyde (p. 50). It combines with sodium bisulphite when it and a saturated solution of the latter are shaken together :

$$C_3H_6O + NaHSO_3 = \underset{\text{Acetone sodium bisulphite.}}{C_3H_6O.NaHSO_3}.$$

EXPT. 45.—Prepare a saturated solution of sodium bisulphite by passing a stream of sulphur dioxide into sodium carbonate crystals covered with a layer of water until the crystals are dissolved. The solution has then an apple green colour. Shake two volumes of acetone with one volume of the bisulphite solution. Crystals of the bisulphite compound separate.

It combines also with phosphorus pentachloride in the same way, losing oxygen which is replaced by chlorine :

$$C_3H_6O + PCl_5 = C_3H_6Cl_2 + POCl_3.$$
Dichloropropane.

EXPT. 46.—Add gradually 10 to 15 grams of phosphorus pentachloride to 5 grams of acetone, cooled in ice. The pentachloride dissolves, and the liquid turns yellow. Pour the product into ice-cold water, and let it stand until the phosphorus oxychloride has decomposed and dissolved. The heavy liquid, which settles to the bottom, and smells like chloroform, is dichloropropane. The dichloropropane distils at 70°.

It also combines like acetaldehyde with phenylhydrazine and hydroxylamine and forms a phenylhydrazone and an oxime (p. 51).

$$C_3H_6O + H_2NOH = C_3H_6{:}NOH + H_2O.$$
Acetoxime.

EXPT. 47.—Mix together in a flask 5 grams of hydroxylamine hydrochloride dissolved in 10 c.c. of water, 3 grams of caustic soda in 10 c.c. of water, and 7 c.c. of acetone and cool. Crystals of acetoxime soon begin to deposit, and the reaction is complete in a few hours, or, if cooled in ice, in a few minutes. Acetoxime melts at 60°.

To prepare the phenylhydrazone the same process may be adopted as in the case of acetaldehyde (p. 51).

Acetone also combines with hydrocyanic acid like acetaldehyde, and forms a cyanhydrin :

$$C_3H_6O + HCN = C_3H_6O.HCN.$$
Acetone cyanhydrin.

Putting these facts together we may draw the conclusion that acetone and acetaldehyde, so far at least as the oxygen is concerned, are similarly constituted, and acetone may therefore be represented by the formula :

$$C_3H_6{:}O.$$
Acetone.

But, on the other hand, acetone has no reducing properties and has no action on either Fehling's solution or ammonia-silver nitrate solution.

The explanation of this difference will have to be deferred until the structure of certain related compounds has been ascertained. For the present it may be stated that it belongs to the group of compounds known as **ketones** (p. 112).

QUESTIONS ON CHAPTER V.

1. Describe the preparation of acetyl chloride. Why is the structure represented by $(CH_3)COCl$?

2. In what manner can an acid chloride be employed to indicate the presence of a hydroxyl group in an organic compound ? Illustrate this by reference to ethyl alcohol.

3. Describe by means of equations the behaviour of acetyl chloride with the following reagents : water, ethyl alcohol, ammonia, sodium amalgam, sodium acetate.

4. Compare the behaviour of ethyl ether and acetic anhydride with different reagents.

5. Describe the materials required and all the operations involved in the preparation of acetic anhydride.

6. What are the sources of acetone ? Compare and contrast the properties of acetone and acetaldehyde.

7. How would you distinguish between acetone and ethyl alcohol, and how could they be separated from a mixture ?

8. How is chloracetic acid obtained ? Describe its behaviour with water, ammonia and potassium cyanide.

9. By what reactions would you obtain the following compounds from acetic acid : acetyl chloride, acetamide, ethyl acetate, acetic anhydride, monochloracetic acid ? Describe briefly the general characters of each of these substances.

10. Calculate the molecular weight of a monobasic acid from the following data : 0·3652 gram of silver salt gave 0·172 gram of silver.

11. Describe three distinct methods of arriving at the molecular weight of acetic acid.

12. How would you prepare a pure specimen of acetic acid from its solution in water ?

CHAPTER VI

METHYL ALCOHOL AND ITS DERIVATIVES

Methyl alcohol is formed with acetic acid and acetone, as already mentioned, in describing the destructive distillation of wood (p. 55). The distillate from the calcium acetate containing the alcohol and acetone is fractionated (methyl alcohol boils at 66° and acetone at 56°) in order to separate the latter from most of the water. The distillate is then dehydrated over quicklime to remove the remainder of the water. A further fractional distillation is required in order to separate the methyl alcohol from the acetone. As a rule, however, a small quantity of acetone is present in commercial methyl alcohol unless the latter undergoes a special treatment for its removal.[1]

On examining the chemical behaviour of methyl alcohol it is at once seen that it bears a very close resemblance to ethyl alcohol. Its molecular formula, as determined by its analysis and its vapour density, is CH_4O. Like ethyl alcohol it forms with sodium, sodium methoxide, CH_3ONa; with hydrochloric acid or phosphorus chloride, methyl chloride, CH_3Cl; with bromine or iodine and red phosphorus, methyl bromide, CH_3Br, and iodide, CH_3I; with sulphuric acid, methyl hydrogen sulphate, $CH_3H.SO_4$; methyl alcohol and sulphuric acid, or sodium methoxide and methyl iodide, yield in the same way dimethyl ether, $(CH_3)_2O$. If, therefore, ethyl alcohol is the hydroxide of the radical **ethyl**, methyl alcohol is the hydroxide of the radical **methyl**, CH_3OH.

[1] A very simple method for removing acetone is to pass into the boiling alcohol (in a vessel attached to a reflux condenser) a current of chlorine and then to distil off the methyl alcohol. The acetone remains as trichloracetone of high boiling point and the alcohol is unattacked.

We can therefore tabulate the following parallel series of derivatives :—

	Methyl.	B.P	Ethyl.	B.P.
Alcohol	CH_3OH	66°	C_2H_5OH	78°
Sodium alcoholate	CH_3ONa	—	C_2H_5ONa	—
Chloride	CH_3Cl	−24°	C_2H_5Cl	12·5°
Bromide	CH_3Br	4·5°	C_2H_5Br	38·5°
Iodide	CH_3I	43°	C_2H_5I	72°
Ether	$(CH_3)_2O$	gas	$(C_2H_5)_2O$	36°
Sulphate	$CH_3.H.SO_4$	—	$C_2H_5.H.SO_4$	—
Nitrate	$CH_3.NO_3$	66°	$C_2H_5.NO_3$	86°
Acetate	$CH_3.C_2H_3O_2$	56°	$C_2H_5.C_2H_3O_2$	78°

In the same way methyl iodide may be made to yield on reduction methane.

Formaldehyde.—Moreover the products of oxidation are similar. Methyl alcohol when oxidised gives **formaldehyde,** just as ethyl alcohol yields acetaldehyde :

$$\underset{\text{Methyl alcohol.}}{CH_3.OH} + O = \underset{\text{Formaldehyde.}}{CH_2O} + H_2O.$$

As in the case of acetaldehyde, formaldehyde may be obtained by oxidising methyl alcohol with oxygen in contact with a surface of platinum.

EXPT. 48.—**Preparation of Formaldehyde.**—The form of apparatus is shown in Fig. 30. The flask *a* contains about 50 c.c. of methyl alcohol. It is provided with a double-bored cork. Through one hole a glass tube passes to the bottom of the flask; and through the second a bent glass tube connects the flask with the short combustion tube *b*. Into the centre of this tube a loose plug of platinised asbestos is inserted, which is kept in position by a short roll of copper gauze, which in turn is held in its place by a slight constriction of the tube. The platinised asbestos is prepared by soaking the loose fibrous asbestos in platinic chloride and gently igniting. The open end of *b* is attached, by a bent tube dipping to the bottom of the flask, to a flask, *c*, cooled in ice. A second tube, *d*, which terminates below the cork is joined to a water-jet aspirator. The flask *a* is warmed in a water-bath to about 40°, and a rapid current of air aspirated through the apparatus. The platinised asbestos is then heated until it begins to glow, after

which the glowing will continue so long as the air current is sufficiently rapid. The liquid which condenses in the flask *c* is a strong solution of formaldehyde in methyl alcohol, and may be used in a similar series of experiments to those described under acetaldehyde (p. 50).

Solutions of formaldehyde, on evaporation *in vacuo*, or in the presence of a little concentrated sulphuric acid, yield a white, crystalline powder, known as **paraformaldehyde,** which has the same percentage composition as formaldehyde, but its molecular

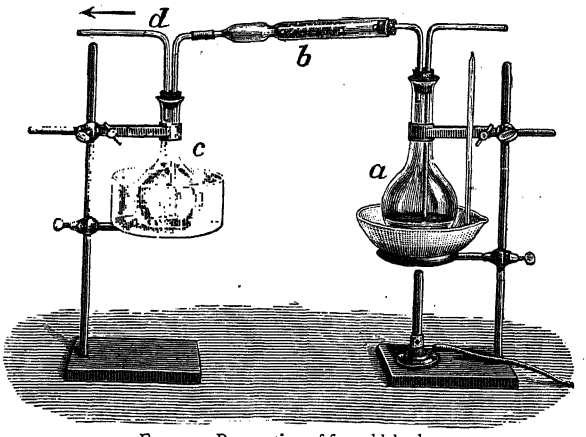


FIG. 30.—Preparation of formaldehyde.

weight is a multiple of that of formaldehyde. The molecular weight of the solid substance has not been ascertained.

Thus formaldehyde, like acetaldehyde, undergoes polymerisation (p. 51).

Technical uses of Formaldehyde.—Since the introduction of formaldehyde as an antiseptic and disinfectant, and for other technical purposes, its manufacture is conducted on a commercial scale. Strong solutions, containing 40 per cent. of the aldehyde dissolved in water containing about 15 per cent. of methyl alcohol, known as **formalin,** as well as the solid paraformaldehyde, or **paraform** are now sold. For disinfecting rooms, the solution may be heated, or the solid paraform volatilised over a lamp. A convenient formaldehyde lamp may be

constructed out of an ordinary spirit-lamp by surrounding the projecting wick with a ball of platinum foil and burning methyl alcohol. The lamp is lighted for a minute and then extinguished, when the platinum continues to glow, evolving formaldehyde.

As an antiseptic, a few drops of the solution will suffice as a preservative for a considerable quantity of material. About 30 milligrams of formaldehyde are sufficient to keep a litre of milk sweet for several days; but its use for this purpose is now prohibited as dangerous to health.

Formaldehyde has the property of rendering gelatine or glue insoluble in water. The aldehyde has in consequence been applied as a substitute for tannin in the leather industry. It has also been employed in a process for the production of artificial silk by exposing finely drawn out threads of glue to formaldehyde vapour, and for waterproofing with egg-albumin, which is then treated with the aldehyde.

EXPT. 49.—The effect of the aldehyde is readily observed by pouring a formaldehyde solution on to a lump of gelatine jelly when the gelatine after some hours becomes insoluble.

Formaldehyde is also employed in the coal-tar colour industry.

Tests for Formaldehyde.—In addition to the ordinary tests, formaldehyde may be detected, when present in very minute quantities, by the following colour reactions.

EXPT. 50.—Add a drop of a 40 per cent. formaldehyde solution to 100 c.c. of water. To this solution add 2 c.c. of a 1 per cent. solution of phenylhydrazine hydrochloride and 1 c.c. of a 5 per cent. potassium ferricyanide solution. On adding a few drops of strong hydrochloric acid a rose-red tint is developed. Another test is to add a few drops of a solution of sodium nitroprusside (p. 215), and a few drops of piperidine (or other secondary base, p. 200), when a deep blue colour is produced. These are extremely sensitive tests.

For the reasons which have been discussed under acetaldehyde, the reactions for formaldehyde point to a similar formula:

$$CH_2{:}O.$$

Formaldehyde.

In one respect formaldehyde differs from acetaldehyde, namely, in its behaviour towards ammonia. Instead of aldehyde-

ammonia, $CH_2O.NH_3$, being formed, a crystalline compound of the formula $(CH_2)_6N_4$, or **hexamethylenetetramine,** is produced.

$$6CH_2O + 4NH_3 = \underset{\text{Hexamethylenetetramine.}}{(CH_2)_6N_4} + 6H_2O.$$

EXPT. 51.—Evaporate in a watch glass on the water-bath a mixture of formaldehyde solution with sufficient strong ammonia to render it alkaline. A crystalline residue remains.

The substance is used in pharmacy under the name of **hexamine.**

When a solution of formaldehyde is mixed with lime-water or magnesia at the ordinary temperature, it is slowly converted into a polymeric substance of the formula $(CH_2O)_6$ or $C_6H_{12}O_6$. The product is a sweet syrup, and its formula and many of its properties indicate a close relationship with grape- and fruit-sugar. It is known as **formose.** The fact has an interesting bearing on the production of the sugars by plants, which takes place during the assimilation of carbon dioxide by their chlorophyll, or green colouring-matter, in presence of sunlight. It has been suggested that in the process the carbon dioxide is reduced to formaldehyde, which then undergoes polymerisation and forms sugar and starch.

Formic acid.—When methyl alcohol or formaldehyde is oxidised it yields formic acid, just as ethyl alcohol when oxidised gives acetic acid :

$$CH_3OH + O_2 = \underset{\text{Formic acid.}}{CH_2O_2} + H_2O.$$

The commercial method of obtaining it is to pass carbon monoxide under pressure into a 10 per cent. solution of caustic soda heated to 160°, when sodium formate is produced :

$$CO + NaOH = \underset{\substack{\text{Sodium}\\\text{formate.}}}{CO_2HNa}.$$

A laboratory method of preparation is based on the decomposition of oxalic acid on heating,

$$\underset{\substack{\text{Oxalic}\\\text{acid.}}}{C_2H_2O_4} = \underset{\substack{\text{Formic}\\\text{acid.}}}{CO_2H_2} + CO_2.$$

a decomposition which, for reasons to be discussed later, occurs much more readily if glycerine is present.

EXPT. 52.—**Preparation of Formic acid.**—Fifty grams of crystallised oxalic acid and 50 grams of glycerine are heated in a retort (250 c.c.) over wire gauze, the retort being connected with a condenser and receiver. A thermometer with its bulb in the liquid is fixed through the tubulus of the retort. The temperature is maintained at 105°–110° until the evolution of gas has slackened, and the liquid then distilled until the temperature reaches 120°. If a larger quantity of formic acid is required, 50 grams more of oxalic acid are added before distilling, and decomposition effected at 105°–110° as before. This process may be repeated. To remove the formic acid remaining in the retort, the contents are transferred to a round flask and distilled in steam (p. 263) until the distillate is no longer acid. The distillate is boiled with excess of lead carbonate and extracted repeatedly with boiling water. On cooling, crystals of lead formate, $(HCO_2)_2Pb$, separate.

Pure formic acid is obtained by passing hydrogen sulphide over the dry lead salt heated to about 110° :

$$\underset{\text{Lead formate.}}{(HCO_2)_2Pb} + H_2S = \underset{\text{Formic acid.}}{2H.CO.OH} + PbS.$$

The lead salt is contained in a wide tube plugged at each end with asbestos. The tube dips downwards so that the free acid runs down and collects in a receiver.

Another reaction of some interest, in which formic acid is produced, is the decomposition of an aqueous solution of hydrocyanic acid which, on standing, yields ammonium formate :

$$HCN + 2H_2O = \underset{\text{Ammonium formate.}}{CO_2H.NH_4}.$$

Formic acid was originally obtained by distilling red ants with water (*formica*=ant) ; the acid is also found in the sting of nettles.

Properties of Formic acid.—Pure formic acid boils at 101° and melts at 8°. It has a pungent and irritating odour and is extremely corrosive, raising blisters on the skin. All formates are more or less soluble in water. Both acid and salts are decomposed with effervescence by concentrated sulphuric acid, yielding carbon monoxide. Pure carbon monoxide is readily obtained in this way.

EXPT. 53.—Heat a little formic acid, or a formate, with conc. sulphuric acid in a test-tube. Effervescence occurs and the escaping carbon monoxide may be ignited:

$$CH_2O_2 - H_2O = CO.$$

Formic acid and the formates are strong reducing agents. A solution of silver nitrate, when heated with the solution of sodium formate, gives a black deposit of metallic silver; mercuric chloride is reduced to the insoluble white mercurous salt, which is precipitated. This reducing action of formic acid, which distinguishes it from all the other fatty acids, will be explained after the structure of the acid has been discussed (p. 78).

EXPT. 54.—Make a solution of sodium formate and divide it between two test-tubes. To one portion add a little silver nitrate solution and to the other some mercuric chloride. On heating, the first solution darkens and gives a deposit of metallic silver, and the second gives a white precipitate of mercurous chloride. The formic acid is oxidised to carbonic acid.

We have seen that oxalic acid is converted into formic acid. The reverse process may be effected by heating dry sodium, or potassium, formate. The alkali salt of oxalic acid is produced, and hydrogen is at the same time evolved (p. 178):

$$\underset{\text{Sodium formate.}}{2CO_2HNa} = \underset{\text{Sodium oxalate.}}{C_2O_4Na_2} + H_2.$$

EXPT. 55.—Heat a few grams of sodium formate in a hard glass test-tube. When the substance begins to fuse and effervesce, the hydrogen which is evolved can be ignited. The presence of sodium oxalate may be detected by extracting with water, acidifying with acetic acid, and adding calcium chloride solution.

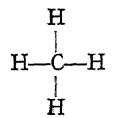
Structure of Methyl alcohol and its derivatives.—The structure of these substances is rendered comparatively simple from the fact that only one carbon atom is present. In looking through the list of compounds derived from methyl alcohol it will be seen that not only is the univalent radical, methyl, linked to a single univalent atom, such as hydrogen and the halogens, or to univalent groups, such as hydroxyl (in methyl alcohol), cyanogen (in methyl cyanide) and hydrogen sulphate (in methyl, hydrogen sulphate), but when the alcohol is oxidised to

the aldehyde the valency of the carbon atom is still maintained by the replacement of two univalent atoms or groups by one bivalent oxygen atom $CH_2{=}O$.

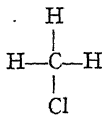
Quadrivalency of Carbon.—Carbon is quadrivalent; that is the atom of carbon is capable of uniting with 4 atoms of a univalent element, 2 atoms of a bivalent element, or 1 atom of a tervalent and 1 of a univalent element. This property of carbon was first recognised by Kekulé, who represented the carbon atom as having 4 bonds or linkages thus:



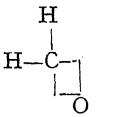
Methane, methyl chloride, formaldehyde, carbon dioxide and hydrocyanic acid will then be represented by **graphic formulæ** as follows



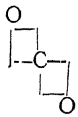
Methane.



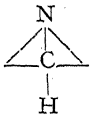
Methyl chloride.



Formaldehyde.



Carbon dioxide.

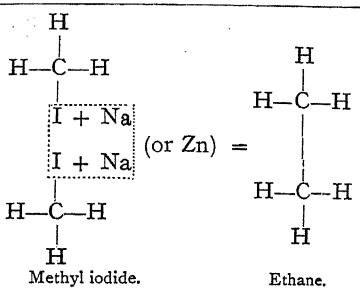


Hydrocyanic acid.

Linking of Carbon atoms.—Kekulé at the same time that he pointed out the quadrivalency of carbon put forward the theory that carbon atoms can unite with one another by means of their bonds. If the two series of alcohols and their derivatives on p. 70 are compared, and, furthermore, if the series of alcohols present in fusel oil (p. 22) is added to the list, it will be noticed that there is the same constant difference, namely CH_2, between successive members:

Methyl alcohol	CH_4O	$>CH_2$
Ethyl alcohol	C_2H_6O	$>CH_2$
Propyl alcohol	C_3H_8O	$>CH_2$
Butyl alcohol	$C_4H_{10}O$	$>CH_2$
Amyl alcohol	$C_5H_{12}O$	$>CH_2$

The same is true of the hydrocarbons CH_4 and C_2H_6. What is the reason of this? The answer is given by turning to the reaction by which methyl iodide is converted by sodium or zinc into ethane (Wurtz). Using structural formulæ the change may be represented as follows:

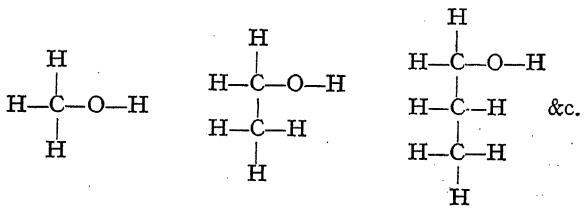


Methyl iodide. Ethane.

It is obvious that no other interpretation of this reaction is at all probable. It follows, therefore, that of the eight bonds of the two carbon atoms, two are utilised in linking the carbon atoms, leaving only six available for hydrogen. And as each additional carbon atom is joined by two bonds to its neighbours on either side it has only two available for hydrogen.

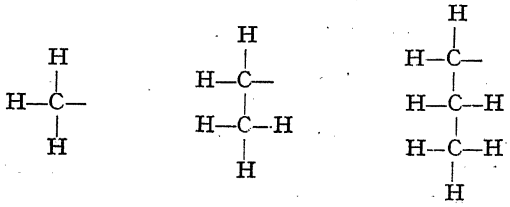
Homologous series.—Therefore each successive member of a series differs from its neighbour by CH_2. Such a series is known as a **homologous series.**

The same is true of the alcohols which may be represented as follows :



CH_4O Methyl alcohol. C_2H_6O Ethyl alcohol. C_3H_8O Propyl alcohol.

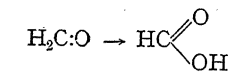
We now see the significance of the univalent radical or alkyl group. It is simply the hydrocarbon group with one free bond.



CH_3' Methyl. C_2H_5' Ethyl. C_3H_7' Propyl.

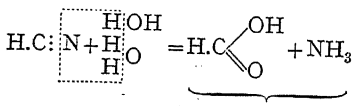
These groups have no free existence. They are merely names used in order to indicate their analogy with hydrogen or sodium in their various combinations.

More about the structure of Acetic and Formic acids.—Before leaving the subject of structure let us return once more to the structural formulæ for formic and acetic acids. Formic acid is obtained by the addition of oxygen to formaldehyde; but at the same time it contains a hydroxyl group like acetic acid. This is interpreted by supposing a hydrogen atom in formaldehyde to be replaced by hydroxyl:



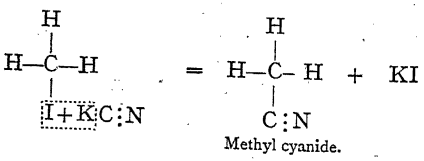
Formaldehyde. Formic acid.

It has been stated that hydrocyanic acid in aqueous solution passes into ammonium formate (p. 74). This change, which is one of great importance, is an example of **hydrolysis**; for it is brought about by the addition of the elements of water to hydrocyanic acid:



Ammonium formate.

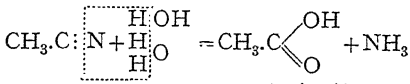
Now methyl cyanide can be obtained, as already pointed out, by heating methyl iodide and potassium cyanide. Written in structural formulæ it will appear as follows:



Methyl cyanide.

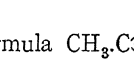
Moreover, it can be hydrolysed like hydrocyanic acid; but water alone has little action. By boiling either with caustic alkali, which unites with the acid formed, or with a mineral acid, which combines with the liberated ammonia, methyl cyanide can be converted into acetic acid. Formulating the

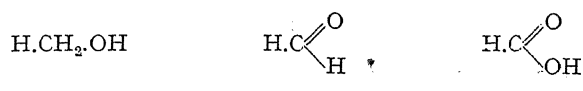
reaction adopted in the case of hydrogen cyanide, the process will appear as follows :



Acetic acid.

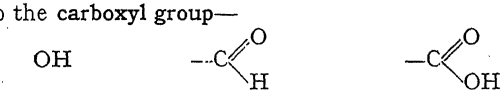
We have thus obtained final evidence of the structure of acetic acid and determined the relative position of each atom.

If this is the structure of acetic acid, then it follows that acetaldehyde has the formula  . The following are three parallel series of alcohols, aldehydes and acids :



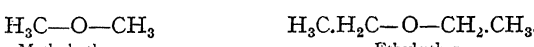
Alcohols. Aldehydes. Acids.

In reviewing these results we may conclude that the properties of an organic compound are mainly determined by the presence of a particular group of atoms. Thus the special property of the alcohols is to be attributed to the presence of the **hydroxyl group**, that of the aldehydes to the **aldehyde group**, that of the acids to the **carboxyl group**—



Hydroxyl group. Aldehyde group. Carboxyl group.

The properties of the ethers in the same way are determined by the **ether group** C—O—C, for this is the essential group in methyl and ethyl ether :



Methyl ether. Ethyl ether.

So far we have confined our attention to compounds containing one and two carbon atoms, and their derivatives ; but a moment's reflection will suggest the possibility of lengthening the chain of carbon atoms attached to the characteristic group,

or, in other words, of introducing larger radicals and multiplying indefinitely the number of members of each class of compounds. This is a perfectly correct deduction, and examples have already been given in the case of a series of alcohols. In the following chapters we shall have to consider other series. The subject is greatly simplified by the fact that as the characteristic group mainly determines the chemical properties of a compound, the lengthening of the radical only affects the physical properties (boiling-point, solubility in water, smell, taste, etc.), and consequently the chemical properties of one member represent those of the whole series.

QUESTIONS ON CHAPTER VI.

1. Discuss the theory which accounts for the existence of homologues among the alcohols.

2. Give a method by which marsh-gas (methane) can be prepared. How would you propose to determine its molecular weight? What relation has the structure of marsh-gas to that of acetic acid?

3. By what process is methyl alcohol obtained? Why is it sometimes termed *methyl hydroxide*?

4. Give an account of the technical uses of formaldehyde. How is it prepared? How is it distinguished from acetaldehyde?

5. By what series of reactions can methyl alcohol be converted into acetic acid?

6. How is formic acid obtained, and how can it be distinguished from acetic acid? In what respects do the acids resemble one another?

7. How are methyl alcohol and acetone separated from crude wood spirit? How would you detect the presence of acetone in commercial methyl alcohol?

8. How can methyl alcohol be converted into (*a*) methane, and (*b*) ethane?

9. Give a full account of the reasons why acetic acid is regarded as a methyl group linked to a carboxyl group.

10. What is meant by Kekulé's "law of the linking of carbon atoms"? How is it applied to the series of alcohols? Give the formulæ.

PART II

THE ALIPHATIC COMPOUNDS

CHAPTER VII

THE PARAFFINS

Paraffins.—Having now learnt something about the methods of purifying organic compounds, of determining their composition, molecular formula, and also something of the principles by which their structure can be ascertained, we will now turn to a group of substances of which certain members have already been mentioned, namely, methane or marsh-gas, CH_4, ethane, C_2H_6, and butane, C_4H_{10}. These are only a few of a long series, of which the lower members (the examples given) are gases; then follow a series of liquids, petroleum spirit, paraffin oil, burning oil and vaseline; and finally, solids constituting paraffin wax. They contain only carbon and hydrogen, being termed, therefore, **hydrocarbons.**

The paraffins occur in nature in large quantities and constitute the raw material of the immense petroleum and paraffin industry. The following table contains a list of these hydrocarbons with their formulæ, melting-points, boiling-points, and specific gravities. They form an excellent illustration of a homologous series. With increasing molecular weight they change their physical properties, passing from gases to liquids and then to solids; but they vary little in their chemical properties. This gradation is characteristic of all such series.

TABLE I.

PARAFFINS—C_nH_{2n+2}.

Formula.	Name.	Melting-point.	Boiling-point.	Specific gravity.
CH_4 .	Methane	− 186°	− 164°	·415 At b.-p.
C_2H_6 .	Ethane	− 172°	− 90°	·446 At 0°
C_3H_8 .	Propane		− 38°	·536 At 0°
C_4H_{10} .	Normal Butane		+ 1°	·600 At 0°
	Isobutane		− 17°	—
C_5H_{12} .	Normal Pentane		+ 36°	·633 At 15°
	Dimethylethylmethane or Isopentane		+ 28°	·627 At 15°
	Tetramethylmethane or Neopentane		+ 10°	
C_6H_{14} .	Normal Hexane		69°	·677 At 0°
	Dimethylisopropylmethane		58°	·679 At 0°
	Dimethylpropylmethane . .		62°	·672 At 0°
	Methyldiethylmethane . .		64°	
	Trimethylethylmethane .		48°	
C_7H_{16} .	Heptane		98°	·700 At 0°
	Isoheptane		90°	·697 At 0°
C_8H_{18} .	Octane		125°	·718 At 0°
C_9H_{20} .	Nonane		150°	·733 At 0°
$C_{10}H_{22}$.	Decane		173°	·745 At 0°
$C_{11}H_{24}$.	Undecane		195°	·774 At the melting-point.
$C_{12}H_{26}$.	Dodecane		214°	·773 At the melting-point.
$C_{13}H_{28}$.	Tridecane		234°	·775 At the melting-point.
$C_{14}H_{30}$.	Tetradecane		252°	·775 At the melting-point.
$C_{15}H_{32}$.	Pentadecane		270°	·776 At the melting-point.
$C_{16}H_{34}$.	Hexadecane	18°	287°	·775 At the melting-point.
$C_{17}H_{36}$	Heptadecane	22°	303°	·777 At the melting-point.
$C_{18}H_{38}$.	Octadecane	28°	317°	·777 At the melting-point.
$C_{19}H_{40}$	Nonadecane	32°	330°	·777 At the melting-point.
$C_{20}H_{42}$	Eicosane	37°	205° At 15 mm. pressure.	778 At the melting-point.
$C_{21}H_{44}$.	Heneicosane	40°	215° At 15 mm. pressure.	·778 At the melting-point.
$C_{22}H_{46}$.	Docosane	44°	224° At 15 mm. pressure.	·778 At the melting-point.
$C_{23}H_{48}$.	Tricosane	48°	234° At 15 mm. pressure.	·779 At the melting-point.
$C_{24}H_{50}$.	Tetracosane	51°	243° At 15 mm. pressure.	·779 At the melting-point.
$C_{27}H_{56}$.	Heptacosane	60°	270° At 15 mm. pressure.	·780 At the melting-point.
$C_{31}H_{64}$.	Hentriacontane	68°	302° At 15 mm. pressure.	·781 At the melting-point.
$C_{32}H_{66}$.	Dotriacontane	70°	310° At 15 mm. pressure.	·781 At the melting-point.
$C_{35}H_{72}$.	Pentatriacontane	75°	331° At 15 mm. pressure.	·782 At the melting-point.

The paraffins are known as **aliphatic hydrocarbons** to distinguish them from **aromatic hydrocarbons** which form a separate group (p. 241). Their derivatives are termed **aliphatic compounds**, from the fact that many important members are found among the fats (ἄλειφαρ, fat), or sometimes derivatives of marsh-gas, which is the simplest representative member of the series. In the same way the aromatic hydrocarbons give rise to the **aromatic compounds** or derivatives of benzene, which is the parent substance of the latter series.

Nomenclature.—The names of the first four members are derived from those of the alcohols containing the same number of carbon atoms, "methyl," "ethyl," "propyl," and "butyl"; the remainder are indicated by the Greek numeral corresponding to the number of carbon atoms present. The names of all the paraffins terminate in "**ane.**" Several members, it will be observed, are represented by two or more substances. These have the same molecular formula but a different grouping of their atoms. They are therefore **isomeric** with one another, and are termed **isomers** or **isomerides.** The difference in atomic arrangement will be discussed later (p. 94).

The paraffins are formed by the natural process of decay of vegetable and animal matter. Marsh-gas, which is found bubbling up from stagnant water, is produced by the action of organisms on cellulose or woody fibre, and the reaction may be represented by the following equation:

$$\underset{\text{Cellulose.}}{(C_6H_{10}O_5)_n} + nH_2O = (3CO_2)_n + \underset{\text{Marsh-gas.}}{(3CH_4)_n}.$$

Paraffins are also formed by the decomposition of animal and vegetable matter by heat, as in the destructive distillation of wood and coal; but the most plentiful source is the petroleum wells.

The Petroleum and Paraffin industry.—The oil deposits found in different parts of the world yield what is known as petroleum, earth oil, rock oil, or mineral oil. The origin of the oil has been variously attributed to the action of steam on the iron carbide of subterraneous mineral deposits (Mendelejeff), which acts like water on aluminium carbide (see p. 92), and to the decomposition at high temperatures and under pressure

of the remains of marine or vegetable life. The petroleum is found in sand or conglomerate known as "sand rocks," and is obtained by boring and pumping.

American petroleum was discovered in 1859 by Colonel Drake, in Pennsylvania. It has since been found in Ohio, Colorado, California, Canada, and other places. The crude oil is carried to the sea coast along iron pipes, some of which are over 1,000 miles long. Here the oil is fractionally distilled in large iron stills and purified. It is divided into the following fractions, which are recognised in the trade by various names:

Name.	Fraction.	Specific gravity at 15°.	Constituents.	Percentage.
	B.-p.			
Cymogene	0°	0·636	—	16·5
Rhigolene	18°		—	
Petroleum ether, or Gasoline	40°–90°	0·642–0·648	C_5H_{12}—C_6H_{14}	
Petroleum naphtha, or Ligroin	90°–120°	0·648–0·692	C_6H_{14}—C_8H_{18}	
Petroleum benzine,[1] or Benzoline	120°–150°	0·692–0·730	C_8H_{18}—C_9H_{20}	
Kerosene, Photogene, or Burning Oil	150°–300°	0·790–0·819	$C_{10}H_{22}$—$C_{16}H_{34}$	54·0
Lubricating oil	—	—	—	17·5
Vaseline	—	—	—	—
	M.p.			
Solid paraffin, or paraffin wax	45°–65°	—	—	2·0

[1] Not to be confused with coal-tar *benzene*.

Cymogene is liquefied by pressure, and by its rapid evaporation lowers the temperature and is used for making ice; **rhigolene** is used in surgery to produce local insensibility by freezing; **petroleum ether** and **ligroin** are used for dissolving and extracting fats and oils; and **benzine** is employed for a similar purpose in dry cleaning. **Petrol,** which is used in internal combustion engines, has a boiling-point of 70°—140° and a specific gravity of 0·705—0·740.

The **kerosene** is purified after distillation by agitating it with concentrated sulphuric acid and afterwards with caustic soda solution and redistilling. The quantity of this fraction may be increased by "cracking," that is, by heating to a high temperature the portions of higher boiling-point, which then break up into products of lower boiling-point. It has a specific gravity

of 0·800—0·870. The annual output is about 2,500 million gallons.

Russian petroleum is found in and around the town of Baku, which stands on the peninsula of Apsheron on the Caspian Sea. The so-called "eternal fires of Baku" attracted the fire-worshippers as early as 600 B.C. Marco Polo described them, and an English traveller, Hanway, in 1754, gave an account of the inflammable vapour with which the ground in the district was saturated.

Systematic working for oil began in 1813, but the output was restricted by Government monopoly, which was abolished in 1872, and in the following year Nobel Brothers started their immense works. The total quantity of oil produced annually is about 2,250 million gallons. The oil differs from American oil, both in its character and in the conditions under which it occurs. It is contained under great pressure, so that in sinking the bore-holes, the oil is frequently driven out to an enormous height. The great Droojba well spouted for four months an oil column from 100 to 300 feet high, which ran to waste, and caused a loss of about 100 million gallons. Occasionally the wells take fire and burn for many weeks. The oil is distilled and purified like the American petroleum. Russian oil contains less of the lower boiling portions than American oil. It consists on the average of:

30 per cent. illuminating oil.
30 per cent. lubricating oil.
35 per cent. solar oil, or ostatki, a heavy oil used for fuel.

and a small quantity of solid paraffin.

The illuminating oil has a higher specific gravity than the American oil (0·820—0·825) (p. 84).

Paraffin industry in Scotland.—The origin of the paraffin industry is due to James Young, who discovered a petroleum spring in Derbyshire in 1848; but the spring shortly afterwards becoming exhausted, he looked about for fresh sources of supply, and found that a bituminous shale occurring in Scotland—the celebrated Torbanehill mineral—would yield paraffin oil on distillation.

The shale is distilled by a continuous process in long vertical retorts, the upper portion of which is of iron and the lower of fireclay, the fresh shale being supplied through the top and the spent shale withdrawn at the bottom. Fig. 31 represents a vertical section of a retort. The inflammable gases, ammonia, and oil pass into the hydraulic main, and thence into coolers where the tar is deposited, the ammonia being collected as in a gas-works, and the inflammable gases used for fuel and illumination. About 30 gallons of oil are obtained from 1 ton of shale. The viscid and tarry-looking oil is redistilled to remove the portions of lower boiling-point, and purified by treatment, first with strong sulphuric acid, and then with caustic soda. It is again distilled, and the distillate is separated into :

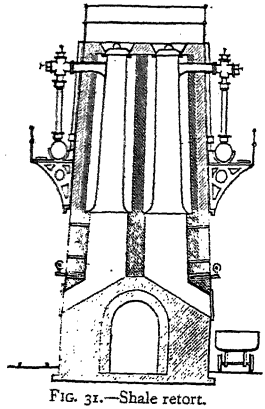


FIG. 31.—Shale retort.

Naphtha.
Burning, or paraffin oil.
Light mineral oil.
Residue.

The residue is treated for paraffin-wax or **scale**. It is first frozen, when it becomes semi-solid, and then passed through a filter press. The filtrate is a viscid liquid, and is used as lubricating oil. The scale is pressed hot to remove adhering oil, and finally **sweated**. This process consists in placing the wax in large cakes on a sloping table in a heated chamber, whereby the lower melting portions run away, leaving behind a much firmer material. The wax is a mixture of paraffins, and melts between 45° and 70°. It is chiefly used in the manufacture of candles. About one-half of the 40,000 tons of paraffin wax produced annually is derived from Scotch shale.

The substance known as **Ozokerite** is found in mines in Galicia, and consists mainly of paraffins. It is used for medical purposes and a preparation of it, resembling beeswax, is sold under the name of **cerasine**.

Petroleum and paraffin oil as illuminants.—The intro-

duction of petroleum and paraffin oil as illuminants has effected a revolution in the construction of lamps. The old Roman lamps, like the one represented in Fig. 32, in which vegetable oil was used, were always shallow vessels, because the low capillarity of the oil restricted its ascent of the wick. If a deep vessel were used, the oil, when exhausted to a certain level, would cause the flame to be extinguished.



FIG. 32.—Terra-cotta lucerna, or Roman lamp from Lanuvium.

EXPT. 56.—The fact just mentioned is easily demonstrated by filling a separating funnel with colza oil (rape seed oil), and inserting a wick into the neck. The wick is lighted, and the oil allowed to trickle out below (Fig. 33). As the level of the oil descends the light is slowly extinguished. In consequence of this, various mechanical contrivances were introduced in more recent times to maintain a constant level in the oil reservoir. The introduction of mineral oil permitted the use of deeper reservoirs.

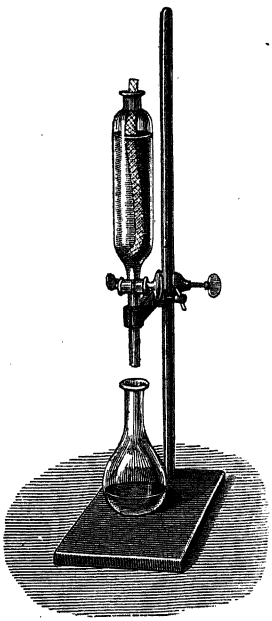


FIG. 33

The luminosity of the flame has, moreover, been greatly intensified by the introduction of flat wicks and glass chimneys, which, by promoting a rapid current of air round the flame, effect more complete combustion, raise the temperature, and thereby increase the luminosity. In consequence of the large consumption of paraffin oil for lamps, and the danger of explosion from the use of too volatile an oil, which may form an explosive mixture with the air inside the reservoir, the Government insist upon a certain standard quality, which is determined by the "flash-point." The standard apparatus is shown in Fig. 34, and the method is known as

Abel's test. The apparatus consists of a cylindrical metal cup, surmounted by a metal cover, holding a slide, which opens or closes apertures in the cover. In moving the slide so as to uncover the central hole, an oscillating lamp is caught by a pin fixed in the slide, and tilted in such a way as to bring the nozzle just below the surface of the lid. When the slide is pushed back so as to cover the hole, the lamp returns to its original position. The vessel is charged to a certain height with the oil to be tested, and a thermometer inserted through the cover, the bulb of which is immersed in the oil. The vessel is heated in a specially constructed water-bath, and as the temperature of the oil rises the slide is occasionally withdrawn, so as to expose the interior of the cup to the jet of flame. When the vapour ignites, the temperature is observed, and this is the flash-point.

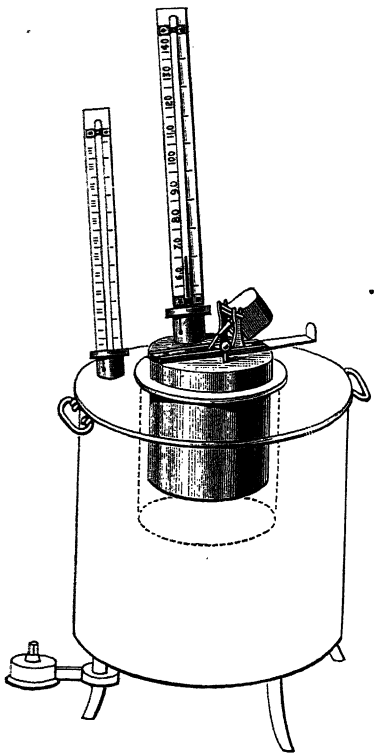


FIG. 34.—The Abel flash-point apparatus.

The lowest flash-point by Abel's apparatus permitted by the Board of Trade is 73° F., but it is now generally recognised that this minimum has been fixed too low.

One of the most common sources of danger in the use of oil lamps is that arising from the burning down of a loosely-fitting and short wick, the lower end of which is not immersed in the oil. Such a wick may smoulder within the reservoir, and

occasionally fire an explosive mixture of paraffin vapour and air. This danger is easily avoided by examining the wick occasionally and renewing it before it becomes too short.

EXPT. 57.—Pour a few c.c. of paraffin oil into a large flask with a wide neck, heat the oil strongly, and blow a little air through with a bellows. If a piece of lighted wick, or roll of paper, be dropped in, a vigorous explosion occurs. There is no danger of shattering the flask.

Physical and chemical properties of Paraffins.—The paraffins are specifically lighter than water, and being insoluble, they float on water. The lower and more volatile members have a peculiar and not unpleasant smell.

Strong and dilute mineral acids have little action on the paraffins, and they are unattacked by oxidising agents. It is owing to this indifference to most reagents that the term paraffin (*parum*, little ; *affinis*, affinity) has been applied.

EXPT. 58.—Shake a little petrol with concentrated sulphuric acid in a test-tube and again with a little strong nitric acid. No heat will be given out, and on pouring the contents of the test-tube into water the petrol will float on the surface unchanged.

Addition and substitution.—Chlorine and bromine, but not iodine, combine directly with the paraffins, and the action is promoted by light. This combination is unlike that usually denoted by the action of chlorine on carbon monoxide in the formation of carbonyl chloride, or phosgene:

$$CO + Cl_2 = \underset{\text{Carbonyl chloride.}}{COCl_2}.$$

Here the molecule of carbon monoxide unites with the molecule of chlorine, without the separation of any part of either molecule. Such a union of molecules produces an **additive,** or **addition,** compound (p. 52). But when chlorine or bromine acts upon a paraffin, hydrochloric or hydrobromic acid is invariably evolved. The rate is greatly accelerated by exposure to light. The action of chlorine on methane is represented as follows:

$$CH_4 + Cl_2 = \underset{\substack{\text{Monochloromethane,}\\ \text{or Methyl chloride,}}}{CH_3Cl} + HCl,$$

and not by the equation:

$$CH_4 + Cl_2 = CH_4Cl_2.$$

EXPT. 59.—(1) Add a few drops of bromine to two test-tubes of petrol. Leave one test-tube in the dark and expose the other to the light. Note the rate at which decolorisation of the bromine occurs. (2) Take a long glass tube closed at one end, fill it with strong brine and invert it in a vessel of brine. Sufficient chlorine is now introduced to fill it one-third full. Mark the height with a strip of paper or rubber ring. Now pass in an equal volume of marsh-gas prepared as described on p. 92, and indicate the level of the liquid by another strip of paper. The apparatus is shown in Fig. 35. It is left in diffused light (bright sunlight may cause an explosion). After several hours the mixed gases will be found to occupy about one-half the original volume. As equal volumes of the two gases contain the same number of molecules, the equation may be written:

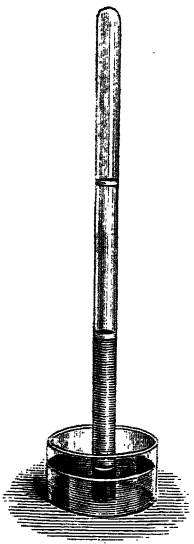


FIG. 35.—Action of chlorine on marsh-gas.

$$\underset{\substack{1\text{ vol.}\\ \text{or }1\text{ mol.}}}{CH_4} + \underset{\substack{1\text{ vol}\\ \text{or }1\text{ mol.}}}{Cl_2} = \underset{\substack{1\text{ vol}\\ \text{or }1\text{ mol.}}}{HCl} + \underset{\substack{1\text{ vol.}\\ \text{or }1\text{ mol.}}}{CH_3Cl}.$$

As hydrochloric acid is absorbed by the brine, only the methyl chloride, CH_3Cl, remains, which occupies half the original volume.

Substitution.—Substances which, like the paraffins, lose hydrogen in the form of hydracid when they enter into combination with the halogens, are termed **saturated** compounds, and the process of replacement of hydrogen by a halogen is termed **substitution.** The products obtained by substitution are known as **substitution products.** The term substitution is not confined to the exchange of hydrogen for chlorine or bromine. The exchange of hydrogen for oxygen or any other element, or of one group of elements for another, is sometimes termed substitution. The process has now lost its original theoretical significance. It played an important part in the overthrow of the dualistic theory.[1]

This process of substitution effected by the action of chlorine on the paraffins will continue, provided enough chlorine is

[1] *Vide* E. von Meyer, *History of Chemistry* (Macmillan).

present, until the whole of the hydrogen is replaced by chlorine. For example, by the further action of chlorine on methyl chloride, the following products are formed:

$$CH_3Cl + Cl_2 = HCl + CH_2Cl_2$$

Dichloromethane, or Methylene chloride.

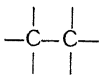
$$CH_2Cl_2 + Cl_2 = HCl + CHCl_3$$

Trichloromethane, or Chloroform.

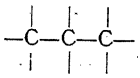
$$CHCl_3 + Cl_2 = HCl + CCl_4$$

Tetrachloromethane, or Carbon tetrachloride.

By the aid of Kekulé's two theories, or principles, which have already been discussed (p. 76), we are able to account for the existence of all the members of the paraffin family, and indeed, of the majority of organic compounds, as we shall presently see. Let us next take the case of two atoms of carbon united or linked together; one bond of each is thereby utilised, leaving six bonds free for union with other atoms:



If these bonds are united to hydrogen atoms, the formula C_2H_6 is obtained, which is that of the second member of the paraffin series. Three carbon atoms utilise four bonds in effecting a linkage between themselves, leaving eight bonds free. Hence the third member of the paraffins is represented by the formula C_3H_8:



If we continue to build up chains of carbon atoms on this principle, we shall find that each end carbon atom of the chain has three available bonds, whereas each of the middle carbon atoms possesses only two. If, therefore, n is the number of carbon atoms present in the compound, there will be $2n$ bonds available for each carbon atom and two extra for the two end carbon atoms, making $2n+2$ available bonds. If, as in the paraffins, these available bonds are attached to hydrogen, the general formula for the paraffins will be C_nH_{2n+2}.

Having now reviewed the chief sources and principal properties of the paraffin family, we will consider in greater detail the characters of a few of the more important members.

Methane, marsh-gas, or **fire-damp,** CH_4, is the only hydrocarbon containing one atom of carbon. It is found rising from stagnant water, and in the gases from oil wells. It is frequently present in coal-pits, especially during a sudden fall in atmospheric pressure, when it diffuses from crevices and old workings. It is also formed by the distillation of coal and forms about 40 per cent. by volume of coal-gas. It is an interesting fact that methane can be obtained by the direct union of carbon and hydrogen at 1200°, or by means of an electric discharge between carbon poles in an atmosphere of hydrogen.

Methane can also be obtained by passing carbon monoxide, or carbon dioxide, mixed with hydrogen, over finely-divided nickel heated to about 300°.

$$CO + 3H_2 = \underset{\text{Methane.}}{CH_4} + H_2O.$$

It is usually prepared by heating together fused potassium or sodium acetate with soda-lime as already described (p. 60):

$$\underset{\text{Sodium acetate.}}{C_2H_3O_2Na} + NaOH = \underset{\text{Methane.}}{CH_4} + Na_2CO_3.$$

But a more convenient method is to decompose aluminium carbide with water.

$$Al_4C_3 + 12H_2O = 3CH_4 + 4Al(OH)_3.$$

EXPT. 60.—**Preparation of Methane.**—The aluminium carbide is spread over a layer of sand in a large flask, furnished with a rubber stopper having two holes and carrying a dropping funnel and delivery tube. Dilute hydrochloric acid is allowed to drop slowly on to the carbide, whereupon methane is evolved, and, after expelling the air, may be collected over water. The gas may be liquefied, if liquid air is available, by drying it through calcium chloride and then passing it through a narrow U-tube, also furnished at the exit end with a drying tube, and cooled in liquid air.

Properties of Methane.—Methane is a colourless gas, without smell. It condenses to a liquid at $-164°$ under a pressure of 760 millimetres. When the pressure is suddenly released, the liquid boils, and then solidifies, the temperature falling to $-186°$.

The sp. gr. of liquid methane at 0° is 0·554. The gas burns with a non-luminous flame and explodes violently when mixed with air or oxygen and fired. Methane shares the general properties of the paraffins in being unaffected by most reagents. Substitution takes place with chlorine and bromine, as already explained (p. 89).

Composition of Methane.—The simplest way of determining the composition of methane is to explode in a eudiometer a measured volume of the gas with an excess of air. The contraction in volume determines the quantity of hydrogen, and the further contraction (on adding potash, to absorb the carbon dioxide) gives the amount of carbon:

$$\underset{\substack{1\text{ vol.,}\\ \text{or }1\text{ mol.}}}{CH_4} + \underset{\substack{2\text{ vols.,}\\ \text{or }2\text{ mols.}}}{2O_2} = \underset{\substack{1\text{ vol.,}\\ \text{or }1\text{ mol.}}}{CO_2} + \underset{\substack{2\text{ vols.,}\\ \text{or }2\text{ mols.}}}{2H_2O}.$$

Now, water-vapour contains its own volume of hydrogen. If, therefore, for 1 volume of methane taken, 2 volumes of gas disappear after explosion, the diminution in volume corresponds to 2 volumes of hydrogen = 2 molecules or 4 atoms of hydrogen.

In the same way, 1 volume, or molecule, of carbon dioxide contains 1 atom of carbon. As every volume of methane gives 1 volume of carbon dioxide, the formula of methane will be CH_4. By this method both the composition and molecular weight of methane are found without previous knowledge of the weight of the constituents or the density of the gas.

Ethane, or **dimethyl,** $CH_3.CH_3$, occurs with methane in the gases from petroleum wells. It is formed by the reduction of ethyl iodide (p. 45) and by the action of sodium or zinc on methyl iodide (p. 77).

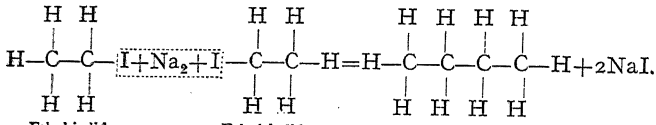
It is a colourless gas which can be liquefied at 4° under a pressure of 46 atmospheres.

Propane, or **ethyl methyl,** $CH_3.CH_2.CH_3$, is also a constituent of petroleum gas. It may be prepared by the reduction of propyl iodide, C_3H_7I, with the zinc–copper couple, or by the action of sodium on a mixture of methyl iodide and ethyl iodide. Both ethane, C_2H_6, and butane, C_4H_{10}, are formed at the same time:

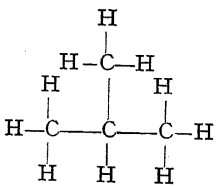
$$\underset{\text{Ethyl iodide.}}{CH_3.CH_2I} + Na_2 + \underset{\text{Methyl iodide.}}{ICH_3} = \underset{\text{Propane.}}{CH_3.CH_2.CH_3} + 2NaI.$$

As in the case of ethane, the structure of propane is confirmed by this synthesis.

Butane, C_4H_{10}.—If reference is made to Table I. (p. 82), it will be noticed that there are two substances with the formula C_4H_{10}, viz. **normal butane** and **isobutane.** The two compounds are therefore isomeric. Their chief difference lies in their boiling-points, normal butane being liquid at $+1°$, whereas isobutane can only be liquefied at the ordinary pressure at $-17°$. Moreover, the products obtained from each by the action of chlorine and bromine have different properties. How is this difference to be accounted for? It is a question of atomic arrangement. The structure of normal butane is determined by synthesis from ethyl iodide and sodium, and has therefore a straight chain of carbon atoms:



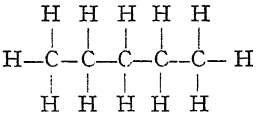
This substance may therefore be termed **diethyl,** $C_2H_5.C_2H_5$. We may consider the formula of normal butane to be derived from that of propane by the addition of a carbon atom, with its accompanying hydrogen atoms, to an end carbon atom of propane. But there is a second possible arrangement of 4 carbon atoms and 10 hydrogen atoms, forming, not a straight, but a branched chain, thus:



This second formula may be derived from propane by attaching a fourth carbon atom to the middle carbon atom of propane. It represents a central carbon atom attached to 3 methyl groups,

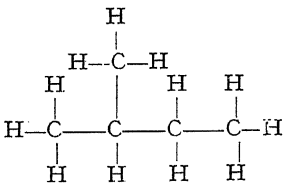
or methane in which 3 hydrogen atoms are replaced by 3 methyl groups. It may therefore be termed **trimethylmethane**, $CH(CH_3)_3$.

Pentane, C_5H_{12}.—This formula stands in Table I. (p. 82) for three compounds, which correspond exactly with the theoretical number of combinations of 5 carbon atoms. One arrangement is produced by adding a fifth carbon atom to one of the end carbon atoms of normal butane:

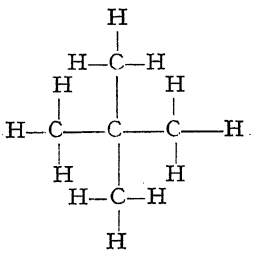


Normal pentane.

This structure is present in normal pentane. Again, the additional carbon atom may be attached either to an end or middle carbon atom of isobutane, and in each case a different grouping will result:



Isopentane.



Neopentane.

The first is called **isopentane**, or **dimethylethylmethane** $C_2H_5.H.C.(CH_3)_2$; the second **neopentane**, or **tetramethylmethane**, $C(CH_3)_4$.

QUESTIONS ON CHAPTER VII

1. Explain why the general formula of the paraffins is represented by C_nH_{2n+2}. What would n be if the vapour density of a paraffin were found to be 57 ?

2. How would you determine the purity of a sample of methane ?

3. Calculate the proportion by volume of methane, hydrogen and nitrogen in a mixture which gave the following data on

analysis :—10 c.c. of gas were made up to 90 c.c. with air and exploded. The volume then measured 73·75 c.c., and after absorption by potash, 69·75 c.c. Temperature and pressure were throughout constant.

4. What is meant by the *flash-point* ? How is it determined ?

5. Write out the structural formulæ of the isomeric hexanes (C_6H_{14}), and name them.

6. Explain the meaning of the terms normal, iso-, and neo-paraffins. How has the structure of ethane been determined ?

7. Give a method by which marsh-gas can be prepared. What are its properties ? How would you obtain pure methane from a sample of coal-gas (methane, hydrogen, carbon monoxide, carbon dioxide, and benzene) ?

8. How would you ascertain the composition and also the molecular weight of marsh-gas ?

9. Discuss the industrial uses of the *paraffins*. What are the natural sources of these substances ?

10. Describe the physical and chemical properties of the paraffins.

11. Explain the following terms : *additive compound, substitution product, saturated hydrocarbon.*

12. What is the chemical character of petrol ? Why does its boiling-point not remain steady as the boiling proceeds ? State what is meant by the *flash-point* of petrol and explain the principles and methods used in its determination.

13. What is meant by the " law of substitution " ? Give some examples showing its application in the determination of the valency of carbon.

14. What are the general properties of the paraffins ? How is ethane prepared ?

15. A mixture of hydrogen, marsh-gas, and nitrogen was mixed with air and exploded, and the residual gas submitted to the action of potash. From the following data calculate the percentage of the three constituents in the original mixture :—

Vol. of mixed gases	14·2 c.c.
Vol. of air added	83·4 ,,
Vol. after explosion	74·2 ,,
Vol. after absorption with potash ...	68·2 ,,

16. The molecular weight of a paraffin was determined by the boiling-point method from the following data : 0·1645 gram dissolved in 8·685 grams of benzene raised the boiling-point 0·135°. (Coefficient for benzene = 26·1.) Give the formula.

CHAPTER VIII

THE HALOGEN COMPOUNDS

The halogen derivatives of the paraffins are formed, as we have seen, by substitution—that is, by the direct action of chlorine and bromine on the paraffins in presence of light. The iodine derivatives cannot be obtained in this way. The inertness of iodine is usually attributed to the liberation during the process of hydriodic acid, which, by its strong reducing action, immediately converts the iodine derivative into the original paraffin. This action is represented in the case of methane as follows:

$$CH_4 + I_2 = CH_3I + HI$$
$$CH_3I + HI = CH_4 + I_2.$$

According to the number of hydrogen atoms of the particular paraffin which are replaced by the halogen, the compounds are known as mono-, di-, tri-, etc., halogen derivatives of that paraffin.

Monohalogen derivatives.—The most important of these substitution products are the monohalogen compounds. The following table contains the names, molecular formulæ, and boiling-points of the first four members. The general formula is $C_nH_{2n+1}X$, in which X stands for the halogen atom.

TABLE II.

MONOHALOGEN DERIVATIVES OF METHANE, ETC., $C_nH_{2n+1}X$.

		B.p.
Methyl chloride, or Chloromethane	CH_3Cl	− 24°
Ethyl chloride, or Chlorethane	C_2H_5Cl	12°·5
Propyl chloride, or Chloropropane	C_3H_7Cl	44°
Isopropyl chloride, or Isochloropropane .	C_3H_7Cl	36°
Methyl bromide, or Bromomethane . . .	CH_3Br	4°·5
Ethyl bromide, or Bromethane	C_2H_5Br	38°
Propyl bromide, or Bromopropane . . .	C_3H_7Br	71°
Isopropyl bromide, or Isobromopropane .	C_3H_7Br	59°
Methyl iodide, or Iodomethane	CH_3I	43°
Ethyl iodide, or Iodethane	C_2H_5I	72°
Propyl iodide, or Iodopropane	C_3H_7I	102°
Isopropyl iodide, or Isoiodopropane . . .	C_3H_7I	89°

The most convenient method for preparing these compounds has already been described (p. 30), namely, by the action of the halogen acid or phosphorus halide on the alcohol, and this method is invariably adopted where the alcohol is available.

Propyl and isopropyl halides.—By reference to Table II. it will be seen that the halogen compounds with 3 carbon atoms exist in two isomeric forms, which are readily distinguished by their properties, boiling-points, specific gravities, etc., and by the nature of their derivatives. The isomerism here is accounted for on the same principle as that of the two isomeric butanes (p. 94). The atom of the halogen, which we may denote by X, may be attached, like one of the methyl groups in butane, either to an end or middle carbon atom:

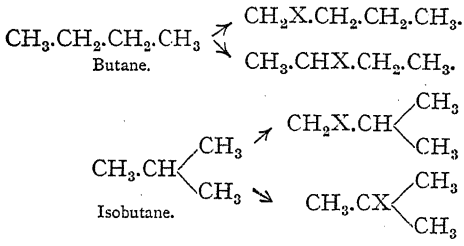
$$CH_3.CH_2.CH_2X. \qquad CH_3.CHX.CH_3.$$

The propyl and isopropyl halides are prepared from the respective alcohols (p. 107); isopropyl iodide is most easily obtained by the action of hydriodic acid on glycerin:

$$\underset{\text{Glycerin.}}{C_3H_8O_3} + 5HI = \underset{\substack{\text{Isopropyl}\\ \text{iodide.}}}{C_3H_7I} + 3H_2O + 2I_2.$$

Butyl halides.—Each of the butyl halides exists in four isomeric forms; the structure of two of these may be

derived from normal butane, and the remaining two from isobutane :



The position occupied by the halogen is of some importance, and is denoted in the following way: when the halogen is attached to an end carbon atom, or is present in a group, $\cdot CH_2X$, the group is called a **primary** group. Where the halogen is attached to a carbon atom linked to not more than two others or, in other words, forms a group :CHX, it is termed a **secondary** group. Similarly, when the halogen is attached to a central carbon linked to three others, it forms a group :CX, which is called a **tertiary** group. In the above example 1 and 3 contain primary, 2 a secondary, and 4 a tertiary group. The position of the halogen is denoted by the use of these terms in conjunction with the name of the paraffin. Both 1 and 3 are primary compounds; but the first is a derivative of normal butane, the second of isobutane. The names run as follows :—

$CH_2X.CH_2.CH_2.CH_3$ normal (primary) butyl halide.
$CH_3.CHX.CH_2.CH_3$ (normal) secondary butyl halide.
$CH_2X.CH(CH_3)_2$ primary isobutyl halide.
$CH_3.CX(CH_3)_2$ tertiary (iso)butyl halide.

The names in brackets may be omitted, as their omission leads to no confusion.

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TABLE III.

DIHALOGEN DERIVATIVES, $C_nH_{2n}X_2$.

		B. p.
Methylene chloride, or Dichloromethane	CH_2Cl_2	41°
Ethylene chloride, or symm. Dichlorethane . .	$C_2H_4Cl_2$	84°
Ethylidene chloride, or unsymm. Dichlorethane .	$C_2H_4Cl_2$	58°
Methylene bromide, etc.	CH_2Br_2	81°
Ethylene bromide, etc.	$C_2H_4Br_2$	131°
Ethylidene bromide, etc.	$C_2H_4Br_2$	110°
Methylene iodide, etc.	CH_2I_2	182°
Ethylene iodide, etc.	$C_2H_4I_2$	M.p. 81°
Ethylidene iodide, etc.	$C_2H_4I_2$	178°

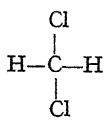
Dihalogen derivatives.—These compounds may be regarded as paraffins in which two atoms of hydrogen are replaced by two atoms of the halogen, or as combinations of a divalent radical with the halogen. Thus, CH_2Cl_2 may be called dichloromethane, or it may be regarded as a compound of the type of calcium chloride, $Ca''Cl_2$, in which the divalent group, CH_2'', plays the part of the calcium atom, and is united to chlorine. The names of the divalent or **alkylene** radicals are derived from the monovalent radicals, with the additional suffix "-ene":

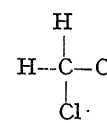
CH_2'' methylene.
C_2H_4'' ethylene.
C_3H_6'' propylene, etc.

The compound CH_2Cl_2 is therefore called methylene chloride.

These radicals are not purely hypothetical groups, like the monovalent radicals; for, with the exception of the first, they represent compounds which exist in the free state. They will be described later (p. 129).

It may be pointed out that the structural formula for methylene chloride admits of two groupings of the atoms:





Yet only one methylene chloride, bromide, and iodide is known. The difficulty is met by supposing that the four bonds

of the carbon atom are not in one plane, but have a space arrangement, represented in Fig. 36, which must be regarded as viewed in perspective.

Only one methylene compound is possible by this structural formula. There are, however, much more weighty reasons for adopting a space arrangement of the 4 carbon bonds, which will be considered later.

Ethylene and ethylidene compounds.—It will be noticed in Table III. (p. 100) that there are two isomeric compounds of the general formula $C_2H_4X_2$, each one of the pair being readily distinguished from the other by its boiling-point. One is formed by the action of the halogen on ethane, and in other ways (p. 52), the other by the union of ethylene with the halogen

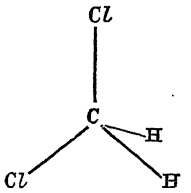


FIG. 36.

(p. 128). The existence of these isomers is at once apparent, if we suppose the two halogen atoms to be differently distributed between the carbon atoms:

$$\begin{array}{l} CH_2X \\ | \\ CH_2X \end{array} \qquad \begin{array}{l} CH_3 \\ | \\ CHX_2 \end{array}$$

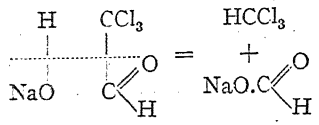
The first is termed an **ethylene** compound, or symmetrical dihalogen derivative of ethane, the second an **ethylidene**, or unsymmetrical compound, ethylene denoting the divalent radical, $CH_2'.CH_2'$, and ethylidene the divalent radical, $CH_3.CH''$.

Trihalogen derivatives.—Two members of this group are of great technical importance. Chloroform, or trichloromethane, and iodoform, or tri-iodomethane, are used in surgery and medicine on an extensive scale.

Chloroform, $CHCl_3$.—This word is derived from the old and obsolete name of the trivalent radical CH''', **formyl.** Chloroform was discovered by Liebig in 1831, and its anæsthetic

action was first pointed out in 1848 by Simpson, who introduced it into surgery. It may be prepared in the pure state by distilling chloral with caustic soda, which yields chloroform and sodium formate.

The structural formula for chloral (trichloracetaldehyde) must at present be accepted. It will be more fully discussed in a subsequent chapter (p. 113).



Chloroform is usually manufactured by boiling ethyl alcohol, or acetone, with bleaching powder and water. The reaction in either case is complex, and probably represents a series of changes. The bleaching-powder may be considered as furnishing both chlorine and lime. The alcohol is converted by the chlorine into chloral, which is then decomposed by the lime, as it is with an alkali, into chloroform and calcium formate:

$$C_2H_6O + 4Cl_2 = \underset{\text{Chloral.}}{C_2Cl_3HO} + 5HCl.$$

EXPT. 61.—**Preparation of Chloroform.**—A round 2-litre flask is fitted with a cork, through which a bent tube passes, connecting the flask with a long condenser and receiver. The flask is placed upon a large sand-bath. The bleaching-powder (200 grams) is ground into a paste with water (800 c.c.). Fifty c.c. of ethyl alcohol or acetone are now added, and the contents heated cautiously until the reaction begins. The flame is removed for a time until the reaction has moderated. The liquid is then boiled until no more heavy drops distil with the water. The distillate is purified by exactly the same process as that described in the preparation of ethyl bromide (p. 30).

Chloroform is a heavy, colourless liquid, b.p. 61°–62°, m.p. −63·2°, and sp. gr. 1·525. It is non-inflammable. When pure, dry chloroform is exposed to sunlight and air, and especially when calcium chloride is present, free chlorine and carbonyl chloride are rapidly formed:

$$2CHCl_3 + 3O = H_2O + 2COCl_2 + Cl_2.$$

The addition of about 1 per cent. of alcohol arrests this change, but even then it is desirable to keep the liquid in the dark, and the bottle filled to the neck.

The presence of the products of the above decomposition is readily ascertained by adding silver nitrate solution, which has no action on pure chloroform, but forms silver chloride when either carbonyl chloride or chlorine is present. For anæsthetic purposes the presence of either impurity is extremely dangerous. Chloroform should leave no residue on evaporation.

The presence of chloroform is detected by its smell. A more delicate test is known as the **phenyl carbamine,** or **isocyanide reaction.** This test depends upon the action of chloroform upon aniline in the presence of caustic potash, which gives phenyl carbamine, a compound with an intolerable smell:

$$CHCl_3 + C_6H_5NH_2 + 3KOH = C_6H_5NC + 3KCl + 3H_2O.$$

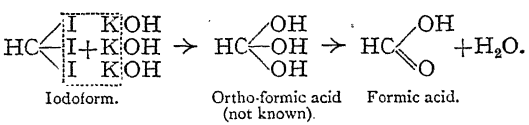
Aniline. Phenyl carbamine.

EXPT. 62.—The following reaction should be performed in a fume cupboard. Bring into a test-tube two drops of chloroform, one drop of aniline, and 1 c.c. of alcoholic potash (caustic potash dissolved in alcohol), and warm. Notice the smell of phenyl carbamine.

Iodoform, CHI_3, is prepared from alcohol or acetone by the action of iodine and an alkali (p. 25). The process is probably analogous to the formation of chloroform.

EXPT. 63.—**Preparation of Iodoform.**—Ten grams of crystallised sodium carbonate are dissolved in 50 c.c. of water. Five c.c. of ethyl alcohol are poured into the solution, and then five grams of iodine gradually added. The liquid is kept at 60°–80°, when iodoform gradually separates out.

Iodoform is decomposed, on boiling with caustic alkalis, into potassium or sodium formate:



Iodoform. Ortho-formic acid (not known). Formic acid.

Hence, in preparing iodoform with caustic alkali in place of the carbonate, it is desirable not to boil the solution.

Iodoform is also prepared commercially by the electrolysis of a solution of potassium iodide in presence of alcohol or acetone. On electrolysis, hydrogen is evolved, and iodine is liberated from the potassium iodide, which, in presence of the alkali, acts upon the alcohol or acetone in the ordinary way.

$$2KI + H_2O = 2KOH + H_2 + I_2.$$

Iodoform crystallises in lemon-yellow, hexagonal plates or star-shaped crystals, which have a characteristic appearance under the microscope. It is used in medicine and surgery as a strong antiseptic and disinfectant; but, on account of its peculiar and unpleasant smell, other organic iodine compounds have been prepared as substitutes. It melts at 119° and at the same time sublimes.

Carbon tetrachloride, CCl_4, is now manufactured on a commercial scale, and is used as a solvent. It is obtained by the action of chlorine on carbon disulphide in the presence of a little metallic iron, which assists the reaction, as a "chlorine carrier":

$$CS_2 + 3Cl_2 = CCl_4 + S_2Cl_2,$$
$$CS_2 + 2S_2Cl_2 = CCl_4 + 6S.$$

Carbon tetrachloride is a colourless liquid, with a sweet smell like chloroform. It boils at 76°–77°. It does not decompose in sunlight like chloroform.

General properties of halogen derivatives.—The physical properties of all the halogen derivatives may be gathered from a study of ethyl bromide, or of chloroform. They possess a sweet, penetrating smell and are specifically heavier than water, in which they are insoluble. They do not burn readily, and indeed some, like chloroform, are not inflammable. A few of them are used as anæsthetics, either for inhaling, like chloroform, or for producing local insensibility by freezing, like methyl and ethyl chloride (p. 28).

Quantitative estimation of halogens—Carius's method. The method of Carius, which is usually employed, consists in oxidising the substance with fuming nitric acid under pressure in presence of silver nitrate. The silver halide which is formed is then separated by filtration and weighed. A thick-walled

tube is sealed at one end, and a few c.c. of fuming nitric acid introduced together with the silver nitrate crystals. The substance is weighed in a narrow tube and slipped in. The tube is then sealed before the blow-pipe in such a way that a thick capillary is formed, which enables it to be subsequently opened (Fig. 37). It is then placed in a hot-air furnace, and is heated for several hours at 200° or above, according to the nature of the compound. The furnace is then allowed to cool, the pressure released before removing the tube, by holding the capillary end in the flame until the glass softens and is perforated by the pressure within. The tube can then be safely opened by cutting with a file in the ordinary way. The contents are washed into a beaker, filtered, washed and the silver halide weighed.



FIG. 37.—Sealed tube used in Carius's method.

Example.—0·151 gram of substance gave 0·134 gram AgBr.

$$\frac{0{\cdot}134 \times 80 \times 100}{188 \times 0{\cdot}151} = 37{\cdot}51 \text{ per cent. of bromine.}$$

QUESTIONS ON CHAPTER VIII.

1. Give the formulæ for any two primary, any two secondary, and any two tertiary, hexyl iodides.

2. Explain the solvent action of boiling caustic potash on iodoform. By analogy, what would be the action of the same alkali on chloroform and carbon tetrachloride ?

3. How would you explain the isomerism and determine the structure of ethylene and ethylidene chlorides ?

4. Explain the formation of chloroform from alcohol and acetone. Give the tests for chloroform.

5. How would you determine the purity of a specimen of chloroform ? What impurities is it likely to contain ?

6. Name the *alkyl* groups in the following formulæ : C_2H_5I ; $CH_3.CHCl.CH_3$; $(CH_3)_2CH.CH_2Br$.

7. Describe and explain the formation of iodoform. What are its chief properties ?

8. How is chloroform prepared ? What reactions prove it to be a derivative of methane ? How can the presence of chlorine be shown ?

9. Suppose a small quantity of chloroform which contains some water has been exposed to sunlight in a large colourless glass bottle, would the chloroform be pure, and, if not, how would you test for the impurities ?

10. Explain the origin of the name ethyl chloride for C_2H_5Cl. What other name is used to designate this substance ?

11. Calculate the weight of silver iodide which would be produced in the quantitative estimation with 0·2 gram of iodoform.

CHAPTER IX

THE ALCOHOLS AND ETHERS

Alcohols.—Of the properties of the alcohols little more need be added to what has already been stated about methyl and ethyl alcohol. A list of the more important alcohols, with their boiling-points and specific gravities, is given in the following table. The term **carbinol** is applied to the carbon group which contains the hydroxyl.

TABLE IV.

THE ALCOHOLS, $C_nH_{2n+2}O$.

		B. p.	Sp. gr.
Methyl alcohol	$CH_3(OH)$	66°	·812
Ethyl alcohol	$C_2H_5(OH)$	78°	·806
Propyl alcohols	$C_3H_7(OH)$		
Primary	$CH_3.CH_2.CH_2(OH)$	97°	·804
Secondary (Isopropyl)	$CH_3.CH(OH).CH_3$	81°	·789
Butyl alcohols	$C_4H_9(OH)$		
Normal primary	$C_2H_5.CH_2.CH_2(OH)$	117°	·810
Normal secondary	$C_2H_5.CH(OH).CH_3$	100°	—
Primary isobutyl	$(CH_3)_2CH.CH_2(OH)$	107°	·806
Tertiary	$(CH_3)_2C(OH).CH_3$	83°	·786
Amyl alcohols	$C_5H_{11}(OH)$		
Normal primary	$C_2H_5.CH_2.CH_2.CH_2(OH)$	138°	·815
Isobutyl carbinol	$(CH_3)_2CH.CH_2.CH_2(OH)$	131°	·810
Secondary butyl carbinol	$CH_3.CH.(C_2H_5).CH_2OH$	128°	—
Methyl propyl carbinol	$C_2H_5.CH_2.CH(OH).CH_3$	119°	—
Methyl isopropyl carbinol	$(CH_3)_2CH.CH(OH).CH_3$	112°	—
Diethyl carbinol	$C_2H_5.CH(OH).C_2H_5$	117°	—
Dimethylethyl carbinol	$(CH_3)_2C(OH).C_2H_5$	102°	—

The isomerism existing among the propyl, butyl and amyl alcohols is due to the disposition of the carbon atoms and the position of the hydroxyl group, and the explanation is precisely the same as that given under the halogen compounds (p. 98).

The higher alcohols.—The above compounds are all liquids, but those with high molecular weight are solids. Some of them are found among natural animal and vegetable products in combination with acids as solid esters which are termed waxes.

Cetyl alcohol, $C_{16}H_{31}.OH$, is combined with palmitic acid in spermaceti, a wax-like substance found in the head of the sperm whale; **ceryl alcohol**, $C_{27}H_{55}.OH$, is found in combination with cerotic acid in Chinese wax, which is used in China for illuminating purposes, and collected from the bark of certain trees, where it is formed through the puncture of an insect; **melissyl** or **miricyl alcohol**, $C_{30}H_{61}.OH$, is combined with palmitic acid in beeswax, and also occurs as a constituent of **carnauba** wax, a yellow, brittle substance, found adhering to the leaves of the Brazilian palm.

The different alcohols do not behave quite alike on oxidation. Methyl and ethyl alcohol form substances known as **aldehydes** (p. 47), but others form a class of compounds known as **ketones** (p. 68). The difference in the behaviour of the alcohols on oxidation separates them into three well-defined groups, the **primary, secondary** and **tertiary** alcohols.

Primary, secondary and tertiary alcohols.—These names are used in the same sense as that applied to the alkyl halides (p. 99). We have only to substitute a hydroxyl group for the halogen atom in the alkyl halides.

A **primary** alcohol has the hydroxyl group linked to an end carbon atom of the series, and contains the group, $.CH_2(OH)$.

A **secondary** alcohol has the hydroxyl group attached to a middle carbon atom of a straight chain, and contains the group $:CH(OH)$.

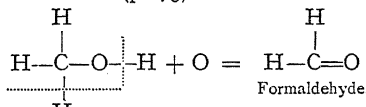
A **tertiary** alcohol contains the group $:C(OH)$, *i.e.* the carbon atom attached to the hydroxyl group is linked to three carbon atoms:

$\cdot CH_2(OH)$, primary alcohol group.
$:CH(OH)$, secondary alcohol group.
$:C(OH)$, tertiary alcohol group.

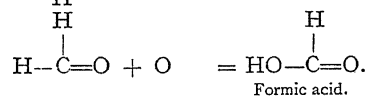
Examples of all three classes will be found in Table IV. (p. 107).

The primary alcohols on oxidation first lose 2 atoms of hydrogen and form **aldehydes**; but the aldehydes can be further oxidised, and, by taking up an additional atom of oxygen, are converted into **acids.**

Thus, methyl alcohol is a primary alcohol and forms formaldehyde and formic acid (p. 73):



Formaldehyde.

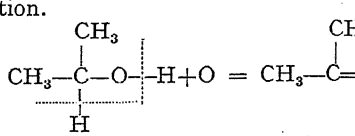


Formic acid.

Ethyl alcohol is also a primary alcohol and forms acetaldehyde and acetic acid.

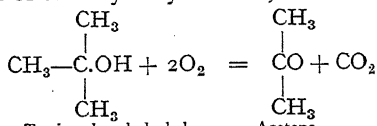
Secondary alcohols also lose 2 atoms of hydrogen; but in this case **ketones** are formed which undergo further oxidation with difficulty, and are therefore not reducing agents (p. 50).

Isopropyl, or secondary propyl alcohol, loses 2 atoms of hydrogen on oxidation in the same manner as methyl alcohol. The product in this case is a ketone, namely, **acetone.** As already pointed out (p. 68), it does not undergo further oxidation very readily and therefore does not reduce Fehling's solution or ammonia-silver nitrate solution.



Secondary propyl alcohol. Dimethyl ketone, or Acetone.

A tertiary alcohol, such as tertiary butyl alcohol, when oxidised breaks up and loses some of its carbon and hydrogen as carbon dioxide and water and gives a ketone with fewer atoms of carbon; in the case of tertiary butyl alcohol, acetone is formed:



Tertiary butyl alcohol. Acetone.

Glycol and Glycerin (glycerol).[1]—It may be pointed out here that just as there are compounds containing more than one halogen atom, there exist others containing more than one hydroxyl group. The most important of these are glycol and glycerol, to which reference will be made later (p. 140):



Glycol. Glycerol.

THE ETHERS

Simple and mixed ethers.—The method of preparing diethyl ether has been described (p. 38). If methylated spirit is used for making ether, a mixture containing a little dimethyl ether, methyl ethyl ether and diethyl ether is obtained and is known as **methylated ether.** The first compound is a gas and the second a very low boiling liquid which evaporates on distillation. If other alcohols are used corresponding substances are obtained. Propyl alcohol gives dipropyl ether and so forth. But, if one alcohol is placed in the vessel with sulphuric acid and another alcohol added from the tap-funnel, an ether with two different radicals is formed. Thus, ethyl and propyl alcohol employed in this manner give ethyl propyl ether:

$$\underset{\text{Ethyl alcohol.}}{C_2H_5.OH} + H_2SO_4 = \underset{\text{Ethyl hydrogen sulphate.}}{C_2H_5.H.SO_4} + H_2O,$$

$$C_2H_5.H.SO_4 + \underset{\text{Propyl alcohol.}}{C_3H_7.OH} = \underset{\text{Ethyl propyl ether.}}{C_2H_5.O.C_3H_7} + H_2SO_4$$

The first kind with two similar radicals are called **simple ethers** and the second, **mixed ethers.**

Metamerism may occur among isomeric ethers, when two different radicals are attached to the oxygen atom. Thus diethyl ether and methyl propyl ether are said to be **metameric:**



$C_4H_{10}O$ Methyl propyl ether. $C_4H_{10}O$ Diethyl ether.

[1] The termination of all alcohols in modern nomenclature is "ol."

Metamerism is therefore defined as a special case of isomerism where different radicals are attached to the same polyvalent element. Other groups of compounds exhibit similar cases of metamerism.

QUESTIONS ON CHAPTER IX

1. Give equations representing the action of chlorine, hydrochloric acid, sodium, calcium chloride, and chromic acid mixture (potassium dichromate and sulphuric acid) respectively upon ethyl alcohol.

2. Give the formulæ for two primary, two secondary, and two tertiary hexyl alcohols and name them. Give also the formulæ and names of their products of oxidation.

3. Name the following: $CH_3.CH(OH).CH_3$; $(CH_3)_2.C(OH).CH_3$; $(CH_3)_2.CH.CH(OH).CH_3$; $(CH_3)_2.C(OH).C_2H_5$.

4. Under what different conditions does sulphuric acid react with alcohol, and what products are formed in the several cases?

5. What products are formed when primary and secondary propyl alcohols are gently oxidised? Compare and contrast their principal properties.

6. A substance having the formula C_3H_8O is thought to be an alcohol. What constitutional formula could such an alcohol have and what would you expect as to its chemical behaviour?

7. How would you determine the constitution of a liquid, the molecular formula of which had been ascertained to be $C_5H_{12}O$?

8. Give two ways of preparing ethyl amyl ether from ethyl and amyl alcohols.

9. Explain and illustrate the term *metameric*.

10. What is *methylated ether*? What impurities does it usually contain?

11. Write the constitutional formulæ for all the different bodies having the molecular formula $C_4H_{10}O$, and indicate by what experiments you would propose to distinguish them.

12. Explain the theory of the preparation of ordinary ether. What bearing has the mode of preparation on the constitutional formula of ether?

13. How is ethyl iodide made, and what is the action of sodium ethylate upon it? Point out the theoretical importance of this reaction.

CHAPTER X

ALDEHYDES AND KETONES

The structure of the aldehydes and ketones.—The similarity and differences existing between the properties of acetaldehyde and acetone have already been pointed out (p. 67). In the method, by which acetone, a typical ketone, is obtained from isopropyl alcohol, we have a means of explaining its structure. Like the aldehydes it contains the same group, C:O, but in the aldehydes the carbon is joined to at least one hydrogen atom, whereas in the ketones it is attached to two radicals.

The aldehydes are characterised by the group HC:O, which is called the **aldehyde group,** the ketones by C:O, which is termed the **ketone group.** The general formula for aldehydes and ketones, where R stands for the radical, is therefore represented as follows:



Aldehyde.



Ketone.

As these radicals are comparatively stable groups we can readily understand the greater stability of the ketones towards oxidising agents.

The aldehydes are named either from the alcohol from which they are derived, or from the acid to which they give rise. $CH_3.CHO$ may be termed ethyl aldehyde or acetaldehyde:

$$\underset{\text{Ethyl alcohol.}}{CH_3.CH_2.OH} \leftarrow \underset{\substack{\text{Ethyl aldehyde}\\ \text{or acetaldehyde.}}}{CH_3.CHO} \rightarrow \underset{\text{Acetic acid.}}{CH_3.CO.OH}$$

The ketones are named from the radicals linked to the ketone group.

The following will serve as examples :

CH_3	C_2H_5	CH_3	C_3H_7
|	|	|	|
CO	CO	CO	CO
|	|	|	|
CH_3	C_2H_5	C_2H_7	C_3H_7
Dimethyl ketone.	Diethyl ketone.	Methyl propyl ketone.	Dipropyl ketone.

Chloral.—A very important derivative of acetaldehyde is chloral, which is used in medicine for inducing sleep. It is trichloracetaldehyde, $CCl_3.CHO$; but it is not usually obtained from the aldehyde by the direct action of chlorine. It was first prepared by Liebig in 1832 by passing chlorine into alcohol, and this is the method which is at present used in its manufacture. The reaction which occurs is not a simple one, and several by-products are formed. The principal product is a solid compound of chloral with alcohol, or **chloral alcoholate**, having the formula $CCl_3.CH(OH).OC_2H_5$. It bears a certain relation to acetal (p. 51). A slow current of chlorine is first passed through cooled ethyl alcohol ; later, the liquid is heated and the current of chlorine continued until no further absorption of the gas takes place. After cooling, chloral alcoholate separates out, and is removed and distilled with concentrated sulphuric acid. Chloral passes over as an oily liquid, and is purified by shaking it with chalk to remove carbonyl chloride and hydrochloric acid.

The series of reactions are represented as follows :

1. $CH_3.CH_2OH + Cl_2 = CH_3.CHO + 2HCl.$
   Acetaldehyde.
2. $CH_3.CHO + 3Cl_2 = CCl_3.CHO + 3HCl.$
   Chloral.
3. $CCl_3.CHO + C_2H_5OH = CCl_3.CH(OH).OC_2H_5.$
   Chloral alcoholate.
4. $CCl_3.CH(OH).OC_2H_5 + H_2SO_4 = CCl_3.CHO + C_2H_5HSO_4 + H_2O.$

Chloral is an oily liquid with a penetrating smell, and boils at 98°. It polymerises, like acetaldehyde, on keeping, or in presence of small quantities of mineral acids, and forms a white, amorphous powder. On adding about one-fifth of its bulk of

water and shaking, great heat is evolved and the mixture solidifies. The solid crystalline substance is **chloral hydrate**, and has the formula $CCl_3.CHO+H_2O$, or more probably $CCl_3.CH(OH)_2$. It dissolves readily in water, and being much more stable than chloral is the compound employed in medicine.

EXPT. 64.—**Preparation of Chloral.**—Chloral may be obtained from chloral hydrate by distillation with concentrated sulphuric acid. Distil 10 grams of chloral hydrate with 5 c.c. of concentrated sulphuric acid in a small distilling flask and collect the colourless liquid distillate. On adding a few drops of water to 2–3 c.c. of the liquid, the solid hydrate is formed with evolution of heat.

When warmed with caustic soda solution chloral hydrate decomposes and a heavy liquid separates. This is **chloroform.** The solution contains sodium formate :

$$\begin{array}{ccccc} CCl_3 & & H & & CHCl_3 \\ | & + & | & = & + \\ CHO & & ONa & & CHO.ONa \end{array}$$

Chloroform. Sodium formate.

QUESTIONS ON CHAPTER X.

1. How would you distinguish between two substances having the formula C_3H_6O ?

2. Give the characteristic reactions of the aldehydes.

3. How would you show that acetone contains 2 methyl groups attached to a CO group ?

4. What are the oxidation products of ethyl propyl ketone ?

5. Name the products of oxidation of primary and secondary propyl alcohol.

6. Describe the preparation of chloral hydrate.

7. How is formaldehyde best prepared ? Give an account of its most striking and useful properties.

8. Describe how you would prepare a specimen of pure acetaldehyde; give an account of its physical properties, and enumerate as many reactions as you can in which it takes part.

9. What is meant by the terms : (*a*) addition-product, (*b*) substitution-product, (*c*) oxidation, (*d*) reduction, (*e*) polymerisation ? Illustrate your answer by the reactions of ordinary acetaldehyde.

10. Give equations illustrating the preparation of chloral

hydrate. Show by graphic formulæ its relation to acetaldehyde, and mention, giving an equation, its decomposition with caustic soda.

11. What are the chief characteristics of the ketones as a class ? To what important changes do they lend themselves ?

12. An organic compound is supposed to be a ketone. Explain precisely how you would prove experimentally that this is the case.

13. An aqueous solution contains either aldehyde, ethyl alcohol, or acetone. How would you distinguish the compound present ?

14. How would you distinguish between an aldehyde and a ketone of the formula C_4H_8O ? Write a list of compounds represented by this formula.

CHAPTER XI

FATTY ACIDS AND THEIR ESTERS

Fatty acids.—In a preceding chapter we have studied two acids, formic and acetic acid. They are the lowest members of a long series, known as **fatty acids** from the fact that many of them are constituents of animal fat and animal and vegetable oils.

The following table contains the names of the first six acids, their derivation, and the names of the acyl radicals :

Name.	Derivation.	Acyl radical.
Formic acid, $H.CO.OH$ . . .	*formica*, an ant	formyl, $H.C:O$
Acetic acid, $CH_3.CO.OH$ . . .	*acetum*, vinegar	acetyl, $CH_3.C:O$
Propionic acid, $C_2H_5.CO.OH$.	πρῶτος, first; πίων, fat	propionyl, $C_2H_5.C:O$
Butyric acid, $C_3H_7.CO.OH$ . .	*butyrum*, butter	butyryl, $C_3H_7.C:O$
Valeric acid, $C_4H_9.CO.OH$ . .	*Valeriana officinalis*, valerian	valeryl, $C_4H_9.C:O$
Capric acid, $C_5H_{11}.CO.OH$ . .	*capra*, a goat	caproyl, $C_5H_{11}.C:O$

General properties of the fatty acids.—They are colourless liquids or solids; the lower members possess a sharp, pungent smell and sour taste, which are absent among the higher members. With increasing molecular weight their solubility in water and also their specific gravity decreases. Formic acid is freely soluble in water and has a specific gravity of 1·231; stearic acid, $C_{18}H_{36}O_2$, is a solid which is non-miscible with water, floats on water and has a greasy feel similar to that of paraffin wax. The chemical properties resemble those of formic and acetic acid.

They are all monobasic acids forming salts with bases and esters with alcohols, whilst the calcium salts on dry distillation yield ketones. They may be represented by the general formula :

$$C_nH_{2n+1}.CO.OH.$$

The sources of formic and acetic acid have already been discussed. Some of the more important sources and uses of the higher members will now be described.

Propionic acid, $C_2H_5.CO.OH$, is most readily obtained by the oxidation of propyl alcohol with potassium dichromate and sulphuric acid. It accompanies acetic acid in pyroligneous acid, and is also found among the products of certain fermentative processes. Although it mixes with water, the acid may be separated from solution by the addition of calcium chloride. The acid then floats as an oily layer on the surface ; for which reason it received the name of propionic acid (*πρῶτος*, first ; *πίων*, fat).

Butyric acid, $C_3H_7.CO.OH$, occurs in two isomeric forms, both of which are found in nature.

Normal butyric acid was discovered in 1814 by Chevreul as a constituent of butter, in which it is present to the extent of about 7 per cent. as the glyceride, or glyceryl ester (p. 121). The smell of rancid butter is due to the decomposition of this ester and the presence of the free acid. It occurs as the free acid in perspiration and in certain animal secretions.

The principal source of the acid is a special kind of fermentation known as the **butyric fermentation,** effected by the combined action of the lactic ferment and the *Bacillus amylobacter* (consisting of slender rods in active movement), on sugar, starch, and other carbohydrates.

This process takes place in several stages. If starch is employed, it is first converted into glucose. The glucose then forms lactic acid (p. 170), and finally the lactic acid decomposes into butyric acid :

$$\underset{\text{Glucose.}}{C_6H_{12}O_6} = 2\underset{\text{Lactic acid.}}{C_3H_6O_3}.$$

$$2C_3H_6O_3 = \underset{\text{Butyric acid,}}{C_4H_8O_2} + 2CO_2 + 2H_2,$$

Isobutyric acid has not been observed in any process of fermentation: but is found either as the free acid or ester in many plants.

The formulæ of these two substances is represented thus [1]:

$CH_3.CH_2.CH_2.CO_2H.$ Butyric acid.

$(CH_3)_2CH.CO_2H.$ Isobutyric acid.

Oils,[2] fats, and waxes.—The nature of these substances was first correctly described by Chevreul (1815–1823), who showed that they were compounds of fatty acids with glycerol. Beef and mutton tallow and lard consist chiefly of the glycerides of stearic acid (*στέαρ*, tallow), $C_{18}H_{36}O_2$, palmitic acid, $C_{16}H_{32}O_2$, and oleic acid, $C_{18}H_{34}O_2$. Oleic acid is not strictly a member of this series of fatty acids. It is called an *unsaturated* fatty acid, as it contains 2 atoms of hydrogen less than stearic acid, which is a *saturated* acid (p. 192); but it is convenient to include it here. The glycerides, as they occur in fat, are known as **stearin** and **palmitin** (75 per cent.), which are solids, and **olein** (25 per cent.), which is liquid at the ordinary temperature. At the body temperature all the fats are liquid:

$$\begin{array}{l} C_{17}H_{35}CO.O.CH_2 \\ | \\ C_{17}H_{35}CO.O.CH \\ | \\ C_{17}H_{35}CO.O.CH_2 \end{array}$$

Formula of Stearin, the glyceride of stearic acid, or glyceryl stearate.

These substances are, however, not confined to the animal fats. Palmitin is the chief constituent of palm oil, olein of olive oil, of which it constitutes 75 per cent., whilst stearin is frequently found in animal and vegetable oils. Butter and cocoa-nut oil contain,

[1] In the replacement of the hydrogen of the alkyl group of a fatty acid by a halogen or radical, the position is denoted by lettering the carbon atoms α, β, γ, δ, beginning with the carbon to which the carboxyl group is attached:

$$\underset{\gamma.}{CH_3}.\underset{\beta.}{CH_2}.\underset{\alpha.}{CH_2}.CO_2H.$$

[2] The term oils used in the present sense implies the vegetable, non-volatile or *fixed oils*, which must be carefully distinguished from the very different class of volatile, or *essential oils* (Part III. p. 269).

in addition to the above, **butyrin**, the glyceride of butyric acid, $C_4H_8O_2$, whilst butter also contains the glycerides of caproic acid, $C_6H_{12}O_2$, caprylic acid, $C_8H_{16}O_2$, and capric acid, $C_{10}H_{20}O_2$. It is difficult to draw any chemical distinction between oils and fats. They consist mainly of glycerides of saturated fatty acids; but the acid may belong, like oleic acid, to a different series. Linseed oil contains the glyceride of linoleic acid, $C_{18}H_{32}O_2$, which has less hydrogen than oleic acid (p. 193). In the waxes the glycerol is replaced by a higher alcohol of the methyl alcohol series, like cetyl alcohol, $C_{16}H_{33}(OH)$, which is combined with palmitic acid in spermaceti (p. 108).

Saponification, as already explained (p. 35), is a special case of hydrolysis and consists in the breaking up of an ester into its two constituent parts, the alcohol and the acid, by the addition of the elements of water.

Manufacture of "stearine" candles.—The so-called "stearine" used in the manufacture of candles is not glyceryl stearate, to which the name is usually applied, but the free acids from fat, separated as far as possible from oleic acid. The fats are hydrolysed by the action of superheated steam in closed boilers, or **autoclaves**, under pressure, with the addition of about 2 per cent. of lime to the fat used. The following equation expresses the reaction in the case of stearin:

$$\begin{array}{l} C_{17}H_{35}CO.OCH_2 \\ C_{17}H_{35}CO.OCH \\ C_{17}H_{35}CO.OCH_2 \\ \quad \text{Stearin.} \end{array} \begin{array}{l} + H.OH \\ + H.OH \\ + H.OH \end{array} = \underset{\text{Stearic acid.}}{3C_{17}H_{35}CO.OH} + \underset{\text{Glycerol.}}{C_3H_5(OH)_3}.$$

After saponification, the "sweet water," which contains the glycerol, is drawn off; a little sulphuric acid is added to decompose the lime salts, and the fatty acids, which float on the surface, are removed, and may be purified by distillation with superheated steam. The acids are pressed hot to remove the liquid oleic acid and a firmer cake is thereby produced. The cake is melted with the addition of a little paraffin wax, and moulded into candles.

Soap manufacture.—The term saponification was originally

applied to the manufacture of soap. **Hard soap** is the sodium salt, **soft soap**, the potassium salt, of the acids of fat. Consequently, caustic soda and caustic potash are always used for the saponification of the fat in soap-making. The reaction which takes place may be illustrated in the case of stearin :

$$\underset{\text{Stearin.}}{(C_{17}H_{35}CO_2)_3C_3H_5} + 3NaOH = \underset{\text{Sodium stearate.}}{3C_{17}H_{35}CO_2Na} + \underset{\text{Glycerol.}}{C_3H_5(OH)_3}.$$

EXPT. 65.—Thirty grams of tallow are placed in a beaker and melted by steam passed in from a flask (with safety tube) containing boiling water. After a short interval, 60 c.c. of a 10 per cent. solution of caustic soda are added and steam driven through until a clear brown solution is obtained. The soap is then separated by the addition of saturated solution of common salt. An alcoholic solution of caustic potash or soda for saponifying oils and fats is much more rapid in its action than an aqueous one, which does not dissolve the fat. Make a ten per cent. solution of caustic soda in methyl alcohol. Place a little lard in a porcelain basin on the water-bath, cover it with the alcoholic soda solution, and stir. When the fat has dissolved, heat for a few minutes to remove the alcohol. A hard mass will remain. It is the sodium salts of the fatty acids mixed with glycerol. It readily dissolves in water. Divide the solution into two portions. To one add dilute hydrochloric acid, when a thick curdy precipitate of the fatty acids separates, which on heating melts and floats on the surface ; on cooling, it becomes a solid cake. To the other portion add strong sodium chloride solution, when a precipitate of the sodium salts of the fatty acids is formed.

The manufacture of soap is carried on in large iron pans, which are heated by steam pipes. Fat, which has been previously "rendered," or melted and strained from cellular tissue, or a mixture of fat and oil, is used. Beef and mutton tallow and olive oil make the best hard, or curd soap. For cheaper soaps, palm oil, palm-nut, cocoa-nut, cotton-seed, and various other vegetable oils, together with rosin (which contains an acid and forms a sodium salt) and oleic acid from the candle industry, are employed. The fat and oil are mixed with caustic soda solution, or "lye," and boiled until hydrolysis is complete, and the materials have become converted into the sodium salts of the fatty acids. Salt is now added, which causes the sodium salts, or soap, to separate as a white granular mass on the surface.

The lower aqueous layer or "spent lyes," containing the glycerol, is drawn off and used for the production of glycerol. The soap is again heated with the addition of a little caustic soda to ensure complete saponification, and the hot, pasty mass, after being allowed to settle two or three days, is run or pumped into frames to cool and set.

Varieties of soap.—**White curd soap** is made from tallow; the different kinds of **yellow soap** usually contain some rosin; **Castile soap** consists largely of sodium oleate, and is made from olive oil; **marine soap** is prepared from cocoa-nut oil, and dissolves in salt water; **transparent soap** is made by dissolving ordinary yellow soap in methylated spirit, and, after driving off the alcohol, pouring out the liquid, which, on cooling, forms a transparent mass; **soft soap** is made by saponifying oil, or fat, with caustic potash. The product in the last case forms a dark-coloured emulsion, which contains excess of alkali and all the glycerol of the original materials; **lead soap**, or lead plaster, is prepared by boiling olive oil with litharge. Some so-called soaps, which are used for cleaning rather than for washing in the ordinary sense, consist chiefly of fine sand, pipe-clay, or fuller's earth, and little real soap. **Dry soap** is made by drying ordinary soap and grinding it with a certain amount of sodium carbonate.

The variety of materials used in the manufacture of soap is so great that the mere proportion of water, alkali, and acid gives no very definite information as to the real value of a soap. Good curd soap for household purposes contains no free alkali, and not more than 30 per cent. of water, which must be regarded as combined water. "Toilet" or "milled" soap, made from compressed shavings of partially dried soap, generally contains much less water. On the other hand, cheap soaps made from cocoa-nut oil, etc., may contain as much as 80 per cent. of water.

Wool-grease, or **Yorkshire grease**, is obtained from the scourings of wool. It forms a brown semi-solid mass, which gives a colourless emulsion with water, and is used as an ointment, known as **lanoline**.

Butter.—Good cow's butter contains on the average about 90 per cent. of fat, 1 per cent. of curd, 1 per cent. of salt, and 8 per cent. of water. Butter fat consists mainly of stearin, palmitin, and olein, with about 7 per cent. of butyrin, and 2 per cent. of caproin, caprylin, and caprin.

Butter substitutes, margarine, oleomargarine.—Beef tallow or suet is heated to a temperature of 35° and subjected to pressure. The lower melting portion, which is expressed, contains a large quantity of olein, and when mixed with certain vegetable oils, and occasionally a little milk and genuine butter, constitutes margarine. The quantity of volatile fatty acid (butyric acid) present as butyrin is always considerably below that in genuine butter. Nevertheless, margarine, if properly prepared, is a perfectly wholesome article of diet.

EXPT. 66.—The difference between butter and margarine may be shown on a small scale by adding to a small quantity of each, in test-tubes, a few c.c. of a methyl alcohol solution of caustic soda and boiling until most of the alcohol is driven off. On cooling and adding dilute hydrochloric acid, the unpleasant smell of butyric acid is given by the butter, but is scarcely noticeable in the case of margarine.

THE ESTERS.

Esters are formed by the action of an alcohol on an organic or inorganic acid, just as salts are produced by the action of a base on an acid (p. 31). Esters may therefore be termed **alkyl salts.**

Methyl alcohol and formic acid, for example, give methyl formate, just as caustic soda and formic acid yield sodium formate:

$$HCO\overline{OH} + \overline{H}OCH_3 = HCO.OCH_3 + H_2O.$$

Methyl formate.

$$HCO\overline{OH} + \overline{H}ONa = H.CO.ONa + H_2O.$$

Sodium formate.

The following are the formulæ of a series of alkyl salts:



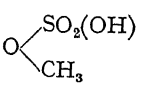
Methyl formate.



Methyl nitrite.



Methyl nitrate.



Methyl hydrogen sulphate.



Methyl chloride.

With the exception of the halide esters like methyl chloride, the alkyl group in the ester is united by oxygen to the acid radical.

Esters of organic acids.— The esters of the fatty acids,

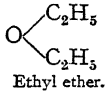
which we shall consider first, were studied in 1782 by Scheele, who discovered a method for their preparation which, with a little modification, is still in general use.

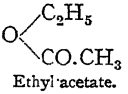
Sources of the esters.—The esters form the sweet-smelling constituents, or **ethereal oils**, of many plants, and on account of their fragrant smell they are manufactured as a substitute for natural perfumes and fruit essences. They may be prepared by the action of an alcohol on an acid chloride, or anhydride (p. 63), or by heating the silver salt of the acid with an alkyl iodide dissolved in ether. Silver acetate and ethyl iodide yield ethyl acetate:

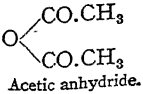
$$CH_3.CO_2Ag + IC_2H_5 = CH_3.CO_2C_2H_5 + AgI.$$

The most common method for preparing esters is the one already described (p. 34), namely, by heating together the acid and the alcohol. The reaction is, however, a reversible one (p. 35). A condition of equilibrium is attained, when a certain ratio exists between the amount of ester and water, and that of free acid and alcohol, and therefore a dehydrating agent must be added. In this respect the action differs from that of an inorganic base on an acid, which is as a rule instantaneous and complete.

Properties of the esters.—The esters are neutral and colourless substances with a fragrant smell, and are, for the most part, liquids which do not mix with water. The methyl and ethyl esters have lower boiling-points than the acids from which they are prepared. The esters in point of structure occupy an intermediate position between the ethers and anhydrides:

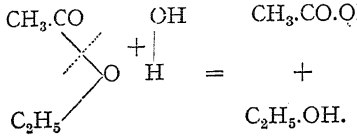

Ethyl ether.


Ethyl acetate.


Acetic anhydride.

In chemical behaviour the esters stand midway between the very stable ethers and unstable anhydrides. The esters are slowly decomposed by water; much more rapidly by caustic alkalis in aqueous solution; still more rapidly by alkalis in alcoholic solution. The process is one of **hydrolysis.** The elements of water are taken up, and the ester is converted

into acid and alcohol. Ethyl acetate gives alcohol and acetic acid:



The reaction is, in fact, identical with the saponification of fats and oils (p. 119), the alcohol in the latter case being glycerol.

The action of ammonia on the esters is essentially different from that of caustic potash or soda; in this case alcohol is formed, but the ammonia remains attached to the acid radical forming an amide (p. 197):

$$\underset{\text{Ethyl acetate.}}{CH_3.CO_2C_2H_5} + NH_3 = \underset{\text{Acetamide.}}{CH_3.CO.NH_2} + \underset{\text{Alcohol.}}{C_2H_5OH}.$$

Isomerism of the esters.—The general formula of the esters of the fatty acids is $C_nH_{2n}O_2$, *i.e.* the same as that of the fatty acids. The esters are readily distinguished from the acids by their neutral reaction, and, in the case of the lower members, by their smell and insolubility in water. Moreover, the esters, unlike the fatty acids, are insoluble in dilute solutions of the alkalis. Among the esters themselves, isomerism may arise from the presence of isomeric acids or alcohols forming the constituent parts of the ester. Examples of this kind of isomerism are ethyl butyrate and ethyl isobutyrate, and propyl and isopropyl acetate. Finally, isomerism may be produced by the union of acids and alcohols to form esters, in which both constituents differ in the different isomers. A compound of the formula $C_4H_8O_2$ may represent methyl propionate, ethyl acetate, or propyl formate:

$C_2H_5.CO.OCH_3$,	Methyl propionate.
$CH_3.CO.OC_2H_5$,	Ethyl acetate.
$H.CO.OC_3H_7$,	Propyl formate.

Such compounds may be readily distinguished by hydrolysis followed by the separation of the alcohol and acid, according to the method described in Expt. 13, p. 35. The alcohol is identified by its boiling-point or other distinctive property;

the acid is tested for in the residue left after removal of the alcohol.

Artificial essences.—It has already been stated that the esters are manufactured as substitutes for natural essences. The following compounds are commonly used for this purpose: ethyl formate (rum), isoamyl acetate (pear), ethyl butyrate (pine-apple), isoamyl isovalerate (apple).

The student is reminded that the constituents of butter (p. 121), fats, oils (p. 118), beeswax, Chinese wax, and spermaceti (p. 108), belong to the group of esters.

QUESTIONS ON CHAPTER XI.

1. Describe the reactions by which fatty acids may be converted into paraffins, aldehydes, and ketones.

2. Define "hydrolysis," and give examples. Name the different ways in which fat may be hydrolysed.

3. Describe briefly the manufacture of soap. How is the water, fatty acid, and alkali estimated in soap?

4. What are the general characters of oils, fats, and waxes?

5. What is the composition of butter and oleomargarine? How can they be distinguished?

6. Give the formula for the *acyl* group in the first six members of the fatty acids.

7. Explain the action of glycerol in the preparation of formic acid.

8. Write precise instructions for the preparation of sodium formate, using oxalic acid as the source.

9. Starting from methyl alcohol, explain, illustrating your answer by equations, how acetic acid can be produced. How can acetic acid be reconverted into methyl alcohol?

10. How has the constitution of the glycerides been determined? State the constitution and the chief constituents of the more important natural fats.

11. Supposing the chief constituent of a soap consisted of sodium stearate, calculate the amount per cent. from the following data: 5 grams dissolved in water to which 50 c.c. normal hydrochloric acid were added required 38 c.c. normal caustic soda solution for neutralisation.

12. A monobasic acid of percentage composition C=54·54, H=9·09, O=36·36 gave the following result on titration:

0·440 gram required 10 c.c. of half-normal caustic soda solution for neutralisation. What is the molecular formula ?

13. In what respect does the action of a metallic base (*e.g.* caustic soda) on an acid differ from that of an alcohol on an organic acid ?

14. Explain the action of (1) caustic potash, (2) ammonia, and (3) sodium on acetic ester.

15. How could you distinguish an acid from an ester, both of which had the same molecular formula, $C_4H_8O_2$? How would you determine the nature of the acid and alcohol combined in an ester of the above formula ?

16. Why is ethyl chloride to be regarded as an ester ?

17. Describe and illustrate two methods of preparing esters of organic acids.

18. Describe the action of water upon ethyl acetate, acetic anhydride, acetyl chloride, and ethyl chloride.

19. By what reactions would you obtain the following derivatives from acetic acid : acetyl chloride, acetamide, ethyl acetate, acetic anhydride, monochloracetic acid ?

20. How is ethyl acetate prepared, and what is its constitutional formula ? Explain clearly why the action of caustic soda on ethyl acetate has been called saponification.

21. Explain clearly what is meant by an ester. How may these bodies be artificially prepared ? How may they be hydrolysed, and what products are obtained by their hydrolysis ?

CHAPTER XII

THE UNSATURATED HYDROCARBONS

The unsaturated hydrocarbons.—There are two important families of unsaturated hydrocarbons—**the olefines** and **acetylenes.** They contain less hydrogen than the paraffins with the same number of carbon atoms, and possess the characteristic property of uniting with other elements, forming **additive** compounds. It is this property which has given rise to the term **unsaturated.**

The most important of the olefines is **ethylene,** formerly called **olefiant gas.** The name olefiant, or oil-forming gas, is connected with a property of the gas already mentioned (and discovered by four Dutch chemists) of uniting with chlorine to form an oily liquid (ethylene chloride, see p. 101). The liquid was known at one time as **Dutch liquid,** and the term **olefiant** has given rise to the word **olefine,** the present name of the family. It may be prepared by the removal of hydrogen bromide from ethyl bromide by means of an alcoholic solution of caustic potash :

$$C_2H_5Br + KOH = \underset{\text{Ethylene.}}{C_2H_4} + KBr + H_2O$$

or, more conveniently, by taking out the elements of water from ethyl alcohol by the aid of concentrated sulphuric acid, phosphoric acid, or other dehydrating agent.

$$C_2H_6O - H_2O = \underset{\text{Ethylene.}}{C_2H_4}$$

The other alcohols behave similarly with the exception of methyl alcohol which does not give methylene, CH_2, a substance never yet isolated, but dimethyl sulphate, $(CH_3)_2SO_4$.

EXPT. 67.—**Preparation of Ethylene.**—Put a little sand or anhydrous aluminium sulphate into a round flask of about 1 litre capacity, pour in 60 c.c. of strong sulphuric acid, and add gradually 20 c.c. of ethyl alcohol. Fit a long, wide, upright tube by a cork to the neck of the flask, and heat the flask and its contents on wire-gauze over a moderate flame. After a time the mixture darkens and effervesces. Ethylene gas is evolved, and, when the air has been expelled, may be ignited at the end of the upright tube, where it burns with a bright, luminous flame. Some of the gas should then be collected in gas bottles over water by means of a delivery tube attached to the flask in which the alcohol and sulphuric acid are heated. The gas bottles must then be stoppered and placed in an upright position. Fill two other gas bottles of the same dimensions, one with chlorine and the other with bromine vapour. Remove the stoppers of the ethylene bottles and replace them by glass plates, and invert over them the bottles of chlorine and bromine from which the stoppers are also removed. On withdrawing the glass plate, the gases mix, and the colour of the chlorine and bromine quickly disappears. Colourless drops of oily liquid are then found on the sides of the bottles; they consist of ethylene chloride in one case and ethylene bromide in the other.

The reactions are expressed by the equations:

$$C_2H_4+Cl_2=C_2H_4Cl_2$$
Ethylene chloride.

$$C_2H_4+Br_2=C_2H_4Br_2$$
Ethylene bromide.

Ethylene combines also with strong (more quickly with fuming) sulphuric acid, forming ethyl hydrogen sulphate (p. 31):

$$C_2H_4+H_2SO_4=C_2H_5.H.SO_4$$
Ethyl hydrogen sulphate.



FIG. 38.

EXPT. 68.—Pour a few c.c. of fuming sulphuric acid into a glass tube about 25 cm. long, closed at one end, introduce ethylene gas until most of the air is displaced, and close with a cork fitted with a glass tap (Fig. 38). On shaking and opening the tap under strong sulphuric acid, the liquid rises nearly to the top of the tube.

This reaction is utilised in estimating the amount

of olefines, or in removing them from a mixture with other gases or liquids, which, like the paraffins, are unabsorbed by the acid.

It may also be employed for preparing the alcohol from the olefine by boiling with water the alkyl hydrogen sulphate obtained by the above process (p. 34) :

$$C_2H_5.H.SO_4+H_2O=C_2H_5OH+H_2SO_4.$$

As coal gas contains about 4—5 per cent. of ethylene this method might be utilised for obtaining alcohol from coal gas. When ethylene mixed with hydrogen is passed over finely divided nickel, hydrogen is absorbed and ethane is formed :

$$\underset{\text{Ethylene.}}{C_2H_4} + H_2 = \underset{\text{Ethane.}}{C_2H_6}$$

Ethylene also unites with the halogen acids, forming ethyl halides :

$$C_2H_4 + HI = \underset{\text{Ethyl Iodide.}}{C_2H_5I}$$

and with hypochlorous acid, giving ethylene chlorhydrin :

$$C_2H_4+HClO=\underset{\text{Ethylene chlorhydrin.}}{C_2H_4Cl(OH)}$$

The following is a list of the more important olefines :—

TABLE V.

THE OLEFINES, C_nH_{2n}.

		Boiling-point.
Ethylene	C_2H_4	-103°
Propylene	C_3H_6	—
Butylene (from butyl alcohol) .	C_4H_8	-5°
Amylene (from isoamyl alcohol)	C_5H_{10}	20–21°

Structure of the olefines.—The readiness with which the olefines unite with other elements to form additive compounds indicates that the full valency of the carbon atoms is not brought into play, which is also the case with aldehydes and ketones. The question then arises : What is the function of the unemployed bonds in an unsaturated compound, and how should they be graphically represented ? Are they inactive or free linkages (Formula I.) such as we usually associate with the formulæ of nitric oxide $-NO$, and carbon monoxide, $=CO$, or, on the other hand, is the residual valency of the carbon atoms engaged in

binding the two carbon atoms together by forming a doul bond (Formula II.) such as we have tacitly assumed to ex between carbon and oxygen in aldehydes and ketones?

Formula I.



Ethylene with free bonds.

Formula II.



Ethylene with double bonds.

The question at first sight seems to have little real significanc Both formulæ explain the transition from unsaturated to sati rated compounds, by the addition of new atoms or groups. I the first, the free bonds are at once brought into action; i the second, one of the double bonds must first be severed. O the other hand, the assumption of free bonds (Formula I. presupposes the existence of substances like methyl, $-CH_3$ or methylene, $=CH_2$, which are unknown, and of two substance having the formula C_2H_4, viz. ethylene and ethylidene:

Ethylene

Ethylidene.

Each of the latter would give rise to a different bromine derivative, viz. ethylene and ethylidene bromide, whereas only one compound, C_2H_4, exists, yielding ethylene bromide.

Theory of the double bond.—The principal grounds upon which the theory of the double bond rests are: firstly, the olefines and, in fact, all unsaturated compounds, unite with an even number of monovalent atoms or groups—in other words, the saturation of one unsaturated carbon atom necessitates that of the other; secondly, the unsaturated carbon atoms invariably adjoin one another. There is an evident connection of a special kind between the two unsaturated carbon atoms, for which the device of the double bond is made to serve.

We must be careful, however, to recognise clearly that the method of indicating this relationship is not taken to imply a firmer connection between the unsaturated carbon atoms, but that, on the contrary, a double bond is a point of weakness in the molecule rather than of strength. Various theories, giving prominence to this idea, have been advanced, resting

mainly on the space arrangement of the carbon bonds (Fig. 36, p. 101). Thus, if we suppose the bonds to diverge at equal angles (109°·5) from the central carbon atom, and to retain their positions when the two carbon atoms are doubly linked, the space arrangement viewed in perspective will appear as in Fig. 39.

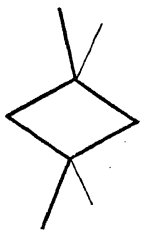


FIG. 39.

If a bond represents the direction in which a force acts, the resultant of two forces acting at an angle of 109°·5 will not be the equivalent of the same forces acting in a straight line. According to another theory, if the result of double linking tends to bend the two pairs of bonds from their original positions into a straight line joining the two carbon atoms, a condition of strain will be set up, which will be a cause of instability (Baeyer's strain theory).

Acetylene, C_2H_2.—Acetylene was first observed by E. Davy (1836), but was more carefully studied by Berthelot (1859), who prepared it by the direct union of carbon and hydrogen by sparking carbon electrodes in an atmosphere of hydrogen. The apparatus used by Berthelot is shown in Fig. 40. It consists of a pear-shaped bulb closed at each end by a double-bored stopper. Carbon electrodes are inserted through two opposite holes of the stopper, whilst, through the other two holes, glass tubes



FIG. 40.—Formation of Acetylene from Carbon and Hydrogen.

are inserted for conducting a current of hydrogen through the bulb. Acetylene is also formed by the incomplete combustion of hydrocarbons; coal-gas, for example, produces acetylene when a Bunsen burner "strikes back" and burns within the metal tube.

EXPT. 68.—Arrange the apparatus shown in Fig. 41. It consists of a glass funnel, bent twice at right angles, and dipping into

a cylinder containing an ammoniacal solution of cuprous chlori
A bunsen burner is lighted at the pinhole jet within the tube, a
placed below the funnel. A current of air is then aspirat
through the apparatus. In a short time a red precipitate of copp
acetylide, $C_2H_2Cu_2O$, is deposited in the cylinder containing t
copper solution. The ammoniacal solution of cuprous chloride
prepared by boiling strong hydrochloric acid with copper oxi
and metallic copper until the liquid is transparent and near
colourless. The solution is then poured into water, and t
precipitate of cuprous chloride is washed once or twice by decan
tation, and then dissolved in a strong solution of ammoniu

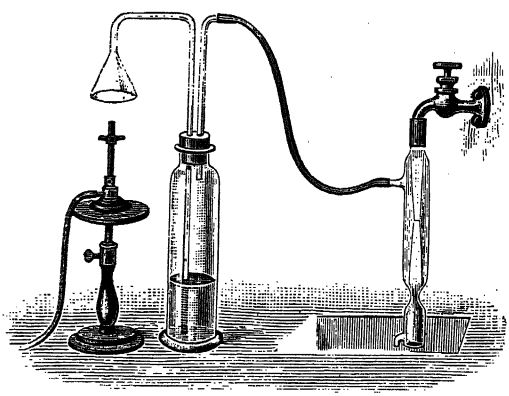


FIG. 41.—Acetylene formed by incomplete combustion of coal-gas.

chloride. When required, a little of the liquid is taken, an
sufficient ammonia is added to give a clear, deep blue solution.

Acetylene is also obtained by the action of alcoholic potas
on ethylene bromide. The process occurs in two steps; mono
bromethylene, or vinyl bromide, is first formed, and the latte
then loses hydrobromic acid and forms acetylene:

$$\begin{matrix}CH_2Br\\|\\CH_2Br\end{matrix} + KOH = \underset{\text{Vinyl bromide, or Monobromethylene.}}{\begin{matrix}CHBr\\\|\\CH_2\end{matrix}} + KBr + H_2O.$$

$$\begin{matrix}CHBr\\\|\\CH_2\end{matrix} + KOH = \underset{\text{Acetylene.}}{\begin{matrix}CH\\\|\|\\CH\end{matrix}} + KBr + H_2O.$$

EXPT. 69.—Fit up an apparatus similar to that drawn in Fig. 42; Allow the gas which is evolved to bubble through an ammoniacal solution of cuprous chloride, contained in a beaker. Pour 50 c.c. of a strong solution (50 per cent., made by dissolving 25 grams of KOH in a few c.c. of water and making up to 50 c.c. with methyl alcohol) of alcoholic caustic potash into the flask, and heat it gently. When ethylene bromide is dropped in from the tap-funnel a rapid evolution of acetylene occurs, and copper acetylide is deposited in the copper solution.

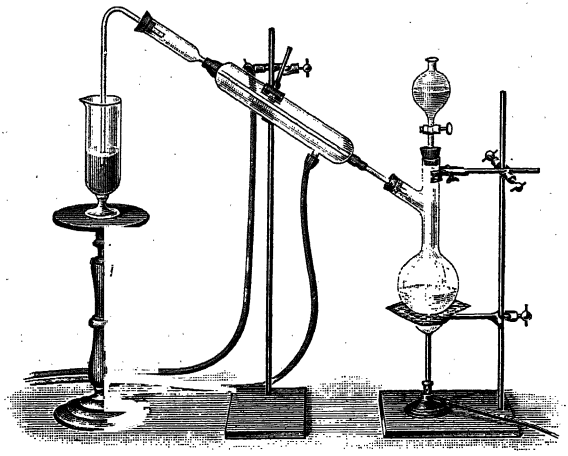


FIG. 42.

Acetylene is now used as an illuminant, and for this purpose is obtained by the action of water upon calcium carbide:

$$CaC_2 + H_2O = C_2H_2 + CaO.$$

Calcium carbide, or calcium acetylide, was first produced commercially by Willson, an American (1892), and was also obtained by the French chemist, Moissan, by the aid of his electric furnace. It is prepared by fusing a mixture of lime and coke by means of a powerful electric current:

$$3C + CaO = \underset{\text{Calcium carbide.}}{CaC_2} + CO.$$

The various electric furnaces in which carbide is manufactured are constructed on the same principle. The heat of the arc,

produced by the passage of the current between the furnac bed which forms the positive electrode and a carbon rod or bundle of rods, which forms the negative electrode, fuse the mixture of coke and lime in which the electrodes are embedded Various forms of furnaces are used, in some of which the charge are introduced and the product removed intermittently; in others the process is continuous, and the fused carbide runs away as it is formed. A carbide furnace in its simplest form is shown in Fig. 43. It consists of a graphite crucible in contact with a metal plate, *a*, which forms the positive electrode, and a carbon rod, *b*, which forms the negative electrode, the intermediate space being filled up with the coke and lime mixture.

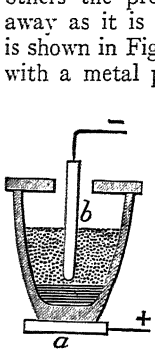


FIG. 43.—Formation of Calcium carbide.

EXPT. 70.—Add a few drops of water to some calcium carbide contained in a test-tube. Rapid effervescence ensues, and the gas, which is evolved, may be lighted at the mouth of the tube. Acetylene burns with a white, intensely luminous and rather smoky flame. The gas obtained from the carbide emits a smell of phosphine, which is due to traces of phosphate in the limestone becoming reduced to calcium phosphide. The latter is decomposed by water, and forms phosphine. For obtaining larger quantities of the gas for experimental illustration, a flask is furnished with a tap-funnel and delivery tube. A layer of sand is placed on the bottom of the flask and small pieces of carbide above this. Water is then added drop by drop from the tap-funnel.

Properties of acetylene.—Acetylene is a colourless gas which, in the pure state, has an unpleasant smell of garlic, quite unlike the smell of a Bunsen burner when it is "burning down," or of the gas given off from commercial carbide. Water dissolves its own volume, and acetone 31 times its own volume, of acetylene at 0° and 760 mm. and 300 times its own volume at 12 atmospheres. This solution, unlike the liquid acetylene, may be safely stored in metal cylinders, and when burnt with oxygen in a blow-pipe flame gives a temperature which readily melts steel and is used for cutting that metal. Acetylene burns with a smoky and very hot flame. For illuminating purposes, complete combustion is effected by using fine pin-hole burners,

which produce a thin, flat flame, having a proportionately large surface. It has about 15 times the illuminating power of coal-gas. Acetylene has been liquefied under a pressure of 26 atmospheres at 0°, and the liquid has a specific gravity of 0·45. It solidifies at −81°. When mixed with air (from 3 to 65 per cent.) and fired, it explodes violently. Even the pure gas, when compressed or in the liquid state, explodes on heating, or by detonation. For illuminating purposes it is therefore necessary to have the gas supply well-cooled. The system upon which the various forms of acetylene generators are constructed is to admit water to the carbide, or to add carbide gradually to the water, and to collect the gas in a gas-holder over water. By the first method the gas-holder, on filling, automatically shuts off the supply of water to the carbide, and so stops the evolution of gas. As the gas-holder empties, fresh water enters the vessel containing the carbide, and the process is repeated until the charge of carbide is exhausted. By the second method, the carbide is added by hand or automatically to a reservoir containing water, from which the gas passes to a gas-holder. Traces of phosphine are generally present in commercial acetylene, and produce, on burning, fumes of phosphorus pentoxide. The phosphine is removed by oxidising agents, such as bleaching powder, chromic acid mixtures, etc.

When acetylene is heated to a red heat, it is completely decomposed into hydrogen and carbon, the latter being deposited as soot. At lower temperatures acetylene appears to polymerise and form benzene, according to the equation:

$$3C_2H_2 = \underset{\text{Benzene.}}{C_6H_6}.$$

A characteristic property of acetylene is the formation of compounds with copper and silver known as **acetylides** of copper and silver. They are deposited as amorphous precipitates by passing the gas into ammoniacal solutions of cuprous chloride and silver nitrate respectively; the copper compound is red, that of silver, white. The substances have the formulæ—

$\underset{\text{Copper acetylide.}}{C_2H_2Cu_2O}.$ $\underset{\text{Silver acetylide.}}{C_2H_2Ag_2O}.$

They are extremely explosive in the dry state, especially the silver compound. When decomposed with potassium cyanide, or hydrochloric acid, acetylene is liberated.

Mono- and di-sodium acetylides, C_2HNa and C_2Na_2, are also known and are obtained by passing the gas over heated sodium.

Additive compounds of acetylene.—Acetylene, like ethylene, forms additive compounds with hydrogen, halogen acids, the halogens, and water.

1. When acetylene mixed with hydrogen is passed over platinum black, or finely divided nickel, at the ordinary temperature, it is converted into ethylene and then into ethane:

$$CH:CH+H_2=CH_2:CH_2.$$
$$CH_2:CH_2+H_2=CH_3.CH_3.$$

2. Acetylene unites with two molecules of halogen acid. The addition occurs in two steps. The two halogen atoms attach themselves to the same carbon atom, and thus form ethylidene compounds:

$$CH:CH+HI=CH_2:CHI.$$
Vinyl iodide.

$$CH_2:CHI+HI=CH_3.CHI_2.$$
Ethylidene iodide.

3. Acetylene is rapidly absorbed by the halogens. Acetylene and bromine form acetylene dibromide and then tetrabromide:

$$CH:CH+Br_2=CHBr:CHBr.$$
Acetylene dibromide.

$$CHBr:CHBr+Br_2=CHBr_2.CHBr_2.$$
Acetylene tetrabromide.

EXPT. 71.—**Preparation of Acetylene tetrabromide.**—Fill a gas-holder with acetylene, and bubble the gas through a U-tube containing bromine cooled in ice. After a time the bromine is decolorised. The heavy, colourless liquid which is formed is acetylene tetrabromide. It is purified like ethyl bromide in Expt. 9, p. 30. **Acetylene tetrachloride,** $C_2H_2Cl_4$, and the **trichloride,** $C_2H_3Cl_3$, are now produced as commercial products for use as solvents, etc.

Structure of the acetylenes.—The acetylenes contain 2 hydrogen atoms less than the olefines, or 4 hydrogen atoms less

than the paraffins. The relation of ethane, ethylene, and acetylene is represented as follows:

C_nH_{2n+2}	C_nH_{2n}	C_nH_{2n-2}
Paraffin.	Olefine.	Acetylene.
C_2H_6	C_2H_4	C_2H_2.
Ethane.	Ethylene.	Acetylene.

For similar reasons to those which have been advanced in the case of the olefines (p. 130), the unsaturated carbon atoms in the acetylenes are assumed to be linked by a treble bond. Thus, each carbon atom of the group has one bond free, which is united to hydrogen or an alkyl group. The union of the unsaturated carbon atoms in the acetylenes is still less stable than that of the double bond in the olefines, and the space arrangement shown in Fig. 44 has the same significance as that represented in the case of the olefines (Fig. 39).

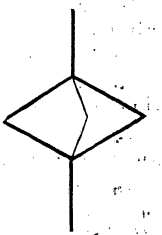


FIG. 44.

In many respects the acetylenes resemble the olefines, but the former undergo change more readily, and generally speaking show less stability.

QUESTIONS ON CHAPTER XII

1. Give a method for preparing ethylene. Name three of its characteristic properties.

2. Devise a method for preparing alcohol from the elements carbon and hydrogen.

3. Compare the properties of the paraffins, olefines, and acetylenes.

4. Describe a method for preparing propylene. What products are obtained when propylene is acted on by bromine, hydriodic acid, and sulphuric acid? Give the structural formulæ of the products.

5. Describe a method for preparing ethylene. How can ethylene be converted into (*a*) ethylene bromide, (*b*) ethyl iodide, (*c*) ethyl hydrogen sulphate, (*d*) ethyl alcohol?

6. Why is ethylene represented as containing carbon atoms united by a double bond?

7. How would you separate ethylene from ethane in a mixture of the two gases, and how would you identify ethylene ?

8. Describe a method by which ethyl iodide may be converted into ethylene, and *vice versa*.

9. In what way can acetylene be distinguished from ethylene ?

10. Explain what is meant by the term unsaturated compound. How are such compounds identified ?

11. Given 10 c.c. of a gas which is either marsh-gas or ethylene, how would you experimentally determine the composition of the gas ?

12. State concisely the chemical reasons for concluding that ethylene should be represented by the formula C_2H_4 and not by the formula CH_2.

13. Draw a diagram of the apparatus required in the preparation of ethylene dibromide, and state the method of procedure.

14. Starting with acetylene, show how ethylene, ethyl alcohol, and so-called cuprous acetylide may be obtained from it.

15. How is acetylene best obtained ? Compare the action of bromine upon this compound with its action on marsh-gas and ethylene respectively.

16. The formula for ethylene is written $CH_2=CH_2$. Give your reasons for preferring this formula to $-CH_2-CH_2-$. What are the general properties of this class of hydrocarbons ? Give examples.

17. Describe the preparation and use of acetylene. How would you distinguish between acetylene and methane and why is the acetylene flame more luminous than that of methane ?

CHAPTER XIII

COMPOUNDS WITH MULTIPLE FUNCTIONS

Polyhydric alcohols.—It was stated on p. 110 that in addition to the alcohols, such as methyl and ethyl alcohol, with one hydroxyl group (monohydric alcohol), other alcohols are known containing more than one of these groups, and are termed **polyhydric alcohols.** Of these alcohols the most interesting are **glycol** or ethylene glycol (dihydric alcohol) and glycerin, or, as it is now commonly called, **glycerol** (trihydric alcohol). In the same way there are compounds containing both hydroxyl and aldehyde or ketone groups which function both as alcohols and also as aldehydes and ketones. This group of hydroxy-aldehydes and -ketones includes the important class of **carbohydrates.** The **hydroxy-acids** in which both alcohol and acid properties are united in the molecule are represented by **lactic, malic, tartaric** and **citric acids.**

Other compounds contain more than one carboxyl group, such as **oxalic, succinic** and **malonic** acids, which are **dibasic acids.**

A further class of compounds containing an ethylene or unsaturated group united to other groups, such as carboxyl, form the important class of unsaturated acids to which **oleic** and **linolsic** acids belong.

These substances will now be considered, and their study is greatly facilitated by the fact that the groups retain to a great extent their individual properties. A hydroxyl group retains the properties it possesses in an alcohol, and a carboxyl group is still acidic as in acetic acid, whatever the other groups present may be.

Glycol (ethylene glycol) was prepared in 1859 by Wurtz and so named by him on account of its sweet taste (γλυκύς, *sweet*). It is obtained from ethylene chloride or bromide by boiling with water in which potassium carbonate is dissolved:

$$\begin{matrix}CH_2Br\\|\\CH_2Br\end{matrix} + H_2O + K_2CO_3 = \begin{matrix}CH_2.OH\\|\\CH_2.OH\end{matrix} + 2KBr + CO_2.$$

The product is then distilled and separated by fractional distillation. It is a viscid liquid which boils at 195°. It is freely soluble in water and possesses in a two-fold degree the properties of an alcohol.

Thus, with sodium it forms a mono- and a di-sodium compound which, boiled with ethyl iodide, yield a mono- and di-ethyl ether, whilst with one or two molecules of acetyl chloride it gives a mono- and di-acetate:

$\begin{matrix}CH_2.ONa\\|\\CH_2.OH\end{matrix}$	$\begin{matrix}CH_2.OC_2H_5\\|\\CH_2.OH\end{matrix}$	$\begin{matrix}CH_2O.COCH_3\\|\\CH_2.OH\end{matrix}$
Sodium glycolate.	Glycol ethyl ether.	Glycol monoacetate.
$\begin{matrix}CH_2.ONa\\|\\CH_2.ONa\end{matrix}$	$\begin{matrix}CH_2.OC_2H_5\\|\\CH_2.OC_2H_5\end{matrix}$	$\begin{matrix}CH_2.O.COCH_3\\|\\CH_2.O.COCH_3\end{matrix}$
Disodium glycolate.	Glycol diethyl ether.	Glycol diacetate.

Hydrochloric acid replaces only one hydroxyl group by chlorine, but phosphorus pentachloride replaces two. The first is ethylene chlorhydrin, the second, ethylene chloride:

$\begin{matrix}CH_2Cl\\|\\CH_2OH\end{matrix}$	$\begin{matrix}CH_2Cl\\|\\CH_2Cl\end{matrix}$
Ethylene chlorhydrin.	Ethylene chloride.

Glycol being a diprimary alcohol, it should yield by successive oxidation of the alcohol groups to aldehyde and carboxyl groups the following series of products:

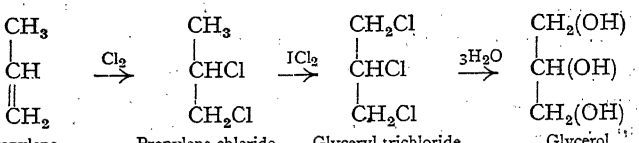
$\begin{matrix}CH_2OH\\|\\CHO\end{matrix}$	$\begin{matrix}CH_2OH\\|\\CO_2H\end{matrix}$	$\begin{matrix}CHO\\|\\CHO\end{matrix}$	$\begin{matrix}CHO\\|\\CO_2H\end{matrix}$	$\begin{matrix}CO_2H\\|\\CO_2H\end{matrix}$
Glycollic aldehyde.	Glycollic acid.	Glyoxal.	Glyoxalic acid.	Oxalic acid.

All these compounds are known, but only three of them, viz., glycollic, glyoxalic, and oxalic acids, have been directly obtained from glycol by oxidation.

Thus, we see that glycol conforms in chemical properties precisely to the behaviour of a compound possessing two primary alcohol groups.

Glycerol, glycerin, or **glyceryl alcohol,**[1] $C_3H_5(OH)_3$.—Glycerol is the only representative of the trihydric alcohols. It was discovered by Scheele in 1779, who found a sweet-tasting liquid separated when olive oil was heated with litharge. It was afterwards observed by Chevreul to be a common constituent of natural fats and oils (p. 118). A small quantity of glycerol is also found among the products of alcoholic fermentation. Glycerol is a viscid, colourless liquid with a sweet taste, which, when pure, crystallises slowly on cooling and then melts at 17°. It boils at 290° with very slight decomposition when pure, and it can be readily distilled with superheated steam or under diminished pressure. It is hygroscopic and mixes with water in all proportions.

The constitution of glycerol has been determined by numerous syntheses. Acetone gives isopropyl alcohol on reduction, and the latter when heated with sulphuric acid forms propylene. Propylene combines with chlorine, giving propylene chloride, which iodine chloride converts into trichloropropane or glyceryl trichloride. When glyceryl chloride is heated with water to 170° it yields glycerol:



Chemical properties of glycerol.—The chemical behaviour of glycerol fully bears out the above constitution. It has the properties of a trihydric alcohol. It forms esters by uniting with 1, 2, and 3 molecules of acetyl chloride. Thus, mono-,

[1] The term *glyceryl* is applied to the trivalent radical, $CH_2'.CH'.CH_2'$.

di-, and tri-acetyl esters are known, and are named respectively mono-, di-, and tri-acetin :

$CH_2.O.CO.CH_3$	$CH_2.O.CO.CH_3$	$CH_2.O.CO.CH_3$
$\vert$	$\vert$	$\vert$
$CHOH$	$CH.O.CO.CH_3$	$CH.O.CO.CH_3$
$\vert$	$\vert$	$\vert$
CH_2OH	CH_2OH	$CH_2.O.CO.CH_3$
Mono-acetin.	Di-acetin.	Tri-acetin.

The glycerides of palmitic, stearic, and oleic acids, which occur in fats, etc., are triacid esters, and should strictly be termed tripalmitin, tristearin, and triolein.

The mono-, di-, and tri-nitrates of glycerol are also known, the last, which is referred to below, being incorrectly named nitroglycerin.

When hydrochloric acid gas is passed into glycerol it is absorbed and forms glycerol α-monochlorhydrin ; if the glycerol is dissolved in acetic acid and heated whilst the gas is passed in, then the dichlorhydrin is produced ; the third hydroxyl group can be replaced by chlorine by the action of phosphorus chloride, the product being glyceryl trichloride, which smells like chloroform. All three substances are liquids :

CH_2OH	CH_2Cl	CH_2Cl
$\vert$	$\vert$	$\vert$
$CHOH$	$CHOH$	$CHCl$
$\vert$	$\vert$	$\vert$
CH_2Cl	CH_2Cl	CH_2Cl
Glycerol α-monochlorhydrin.	Glycerol αα-dichlorhydrin.	Glyceryl trichloride.

The products of oxidation of glycerol, theoretically possible, are very numerous, and many of them have been obtained either directly or indirectly from glycerol. Glycerol contains two primary and one secondary alcohol groups. The two primary groups should yield successively aldehyde and carboxyl groups ; the secondary, a ketone group. By the action of dilute nitric acid on glycerol, glyceric and tartronic acids have been obtained. On further oxidation oxalic is formed :

CH_2OH	$CO.OH$
$\vert$	$\vert$
$CHOH$	$CH.OH$
$\vert$	$\vert$
$CO.OH$	$CO.OH$
Glyceric acid.	Tartronic acid.

By heating glycerol with potassium hydrogen sulphate it loses the elements of water and gives **acrolein**, which has the acrid and penetrating smell of burnt fat, the latter being due to the decomposition of the glycerol of the fat:

$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} \quad -2H_2O = \quad \begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CHO \end{array}$$

Acrolein.

EXPT. 72.—Heat in a test-tube 5 c.c. of glycerol with 1 gram of powdered potassium hydrogen sulphate and notice the smell.

Acrolein is a colourless liquid which boils at 52°. It has the properties of an aldehyde, reducing alkaline solutions of silver and copper, whilst its olefine character is shown by its union with the halogens and halogen acids:

$$CH_2{:}CH.CHO + Br_2 = CH_2Br.CHBr.CHO.$$

Bromine is immediately decolorised. On oxidation acrolein is converted into acrylic acid (p. 192).

Manufacture of glycerol.—Glycerol is manufactured on a large scale for a great variety of industrial purposes. The chief sources are the fats and oils and spent lyes of the soap works. It has already been stated (p. 119) that the fats and oils are usually hydrolysed either with a little strong sulphuric acid, or by superheated steam, in the presence of a small quantity of lime. In the sulphuric acid process, which is used for the poorer qualities of fat and oil, some of the glycerol is decomposed by the acid, but the remainder is recovered from the liquors from which the fatty acids have been separated. In the lime process, the "sweet water" which contains the glycerol is concentrated, filtered through animal charcoal to remove colouring matter, and evaporated to the requisite specific gravity. The spent lyes of the soap works, containing 5 to 8 per cent. of glycerol, were until recently a waste-product. At the present time they are the main source of the glycerol used in commerce.

Glycerol is usually purified by distillation with superheated steam. The distillate, which contains water, is evaporated to the

requisite consistency in steam-heated vacuum pans, *i.e.* vessels from which the air is partially exhausted. In this way evaporation can be rapidly effected at a temperature at which no decomposition or discoloration of the glycerol can occur.

Glycerol combines with metaphosphoric acid to form glycerol-phosphoric acid :

$$C_3H_5(OH)_3 + HPO_3 = C_3H_5(OH)_2O.P(OH)_2,$$

the salts of which are used as tonics in medicine. But the greater part of the distilled glycerol is used in the manufacture of nitroglycerin.

Nitroglycerin, Glyceryl trinitrate, Nobel's oil, $C_3H_5(ONO_2)_3$. —The formation of nitroglycerin by the action of nitric acid on glycerol was discovered by Sobrero in 1846, but the practical application of this discovery to the manufacture of explosives is due to Nobel, a Swedish engineer (1862). Nitroglycerin is prepared by mixing 12 parts of fuming nitric acid and 20 parts of sulphuric acid and injecting into the well-cooled acid mixture a spray of glycerol (4 parts), which is forced in by a current of air :

$$C_3H_5(OH)_3 + 3HNO_3 = \underset{\substack{\text{Glyceryl nitrate, or}\\ \text{Nitroglycerin.}}}{C_3H_5(ONO_2)_3} + 3H_2O.$$

The sulphuric acid serves to unite with the water which is formed in the reaction. The mixture is allowed to stand, and the nitroglycerin, which forms a layer on the surface, is run into water, from which it separates as a heavy oil. It is well mixed with the water and then with a solution of sodium carbonate to remove all trace of acid, which, if present, renders the substance liable to decompose and explode. It is finally freed from water by filtering through flannel or felt covered with a layer of salt.

Properties of nitroglycerin.—Nitroglycerin is a heavy, colourless liquid of specific gravity 1·6, which solidifies at 8°. It has a sweetish, burning taste, and is poisonous. In minute doses it is used in medicine. When spread in a thin layer over a large surface, it may be ignited without danger, and burns quietly ; but when suddenly heated, it explodes like most of the

nitric esters. A more violent explosion is produced by detonation.

The uncertainty which first attended the use of the oil as an explosive led to the discovery that the admixture of inert absorbent materials, whilst increasing the explosive force, rendered the nitroglycerin less sensitive and more easily manipulated.

Dynamite is made by mixing 3 parts of nitroglycerin with 1 part of **kieselguhr,** a fine siliceous earth which is very light and porous, and can absorb considerable quantities of nitroglycerin without becoming pasty. The mixture is moulded and compressed into cartridges and fired by a detonator (mercury fulminate). **Blasting gelatine** is made by dissolving 7 parts of nitrated cellulose (p. 166) in 93 parts of nitroglycerin, and forms a solid translucent mass. **Cordite** is prepared from nitroglycerin (18 parts) and gun-cotton (73 parts) made into a pulp with acetone, to which a little vaseline is added. The pulp is squeezed through small holes into threads from which the acetone evaporates, and the threads are cut up and used for smokeless rifle cartridges. A great number of explosives are prepared containing nitroglycerin mixed with such substances as sawdust, charcoal, nitrates of potassium and ammonium, etc., and are known as **forcite, vulcan powder, lithofracteur, etc.**

The method of preparing nitroglycerin resembles that of ethyl nitrate from ethyl alcohol and nitric acid. Nitroglycerin is in fact an ester and not a nitro-compound (p. 35), and like an ester it is hydrolysed by caustic alkalis :

$$C_3H_5(ONO_2)_3 + 3KOH = C_3H_5(OH)_3 + 3KNO_3.$$

The name nitroglycerin is therefore a misnomer, but it has become established through usage as the technical name of the compound.

QUESTIONS ON CHAPTER XIII

1. Give examples of a di- and tri-hydric alcohol.

2. How is glycol obtained ? Compare the physical and chemical properties of ethyl alcohol and ethylene glycol.

3. What is the action of water and a metallic oxide on ethylidene chloride ? What relation does *acetal* bear to glycol ?

4. Give a list of all the possible oxidation products of ethylen glycol. Which of these have been actually obtained from th glycol ?

5. Explain why glycol is regarded as a di-primary alcohol.

6. How has glycerol been obtained synthetically ?

7. What is nitroglycerin and how is it obtained ? Is th substance correctly described as a nitro-compound ? Give you reasons.

8. Common alcohol is spoken of as a primary monohydri alcohol ; explain the meaning of this designation.

9. How is glycerol obtained ? Describe the action upon it o hydriodic acid, hydrochloric acid, oxalic acid, nitric acid, acety chloride. What substance is formed on heating glycerol ?

10. What are the natural sources of glycerol and how is it obtained on the industrial scale ? How can it be shown that glycerol is a trihydric alcohol, and what products are obtainable by its oxidation ?

11. Glycerol is called a trihydric alcohol. In what way does its behaviour justify the name ? How would you distinguish glycerol from a syrup made from glucose or cane-sugar ?

12. Enumerate the substances which may be obtained directly from glycerol and express the reactions by equations.

CHAPTER XIV

THE CARBOHYDRATES

The carbohydrates.—The most important members of the family of hydroxy-aldehydes and ketones are the *pentoses* and *hexoses* (so called from the number of carbon atoms), which, together with certain related compounds of a highly complex structure, are grouped together under the name of **carbohydrates.**

The carbohydrates are among the chief products of plant life, and are also found, but less extensively, in the animal kingdom. Grape-sugar, fruit-sugar, cane-sugar, starch, cellulose, and the gums are vegetable products, whilst milk-sugar, glycogen, and, occasionally, grape-sugar, are derived from the animal organism. The study of their formation and decomposition in the living organism belongs to the domain of plant and animal physiology. Organic chemistry is concerned with their chemical changes outside the body.

The wide distribution of the carbohydrates, their extensive consumption as food, and their employment in various industries (as in the manufacture of fabrics and paper and in the production of alcohol) have given them an interest and importance possessed by few other groups of organic compounds.

Some of the carbohydrates, like cane- and grape-sugar, are crystalline, soluble in water, and sweet; whilst others, like starch and cellulose, are tasteless, insoluble in water, and possess an organised structure. Although these two groups show marked differences in physical properties, they are, nevertheless, closely related chemically. The majority contain hydrogen and oxygen in the proportion found in water, so that their composition may be expressed by the formula $C_x(H_2O)_y$. This fact has given rise to the name hydrate of carbon, or carbohydrate. The

more complex members are readily hydrolysed by acids c hydrolytic enzymes (p. 23) into one or more of the simple members. Thus, starch and cellulose, on boiling with dilut sulphuric acid, are both converted into grape-sugar:

$$\underset{\text{Starch or Cellulose.}}{(C_6H_{10}O_5)_n} + nH_2O = \underset{\text{Grape-sugar.}}{nC_6H_{12}O_6}.$$

Classification of the carbohydrates.—The carbohydrate fall naturally into two classes, as explained above; the swee and crystalline substances form one class, termed **sugars**, an the tasteless and non-crystalline compounds belong to the other The sugars are further divisible into two principal groups of a more or less complex molecular formula. There are three groups, therefore—which are distinguished by the names **monosaccharoses**, with 5 and 6 carbon atoms, of the general formulæ $C_5H_{10}O_5$ and $C_6H_{12}O_6$; the **disaccharoses**, with 12 carbon atoms, of the general formula $C_{12}H_{22}O_{11}$; (there is also a trisaccharose of the formula $C_{18}H_{32}O_{16}$;) and the **polysaccharoses** of unknown but high molecular weight, possessing the empirical formula $C_6H_{10}O_5$, usually written $(C_6H_{10}O_5)_n$.

Table VI. contains a list of the more important natural carbohydrates.

TABLE VI.

THE NATURAL CARBOHYDRATES.

THE SUGARS.		
Monosaccharoses, *Pentoses*, $C_5H_{10}O_5$,	*Disaccharoses*, $C_{12}H_{22}O_{11}$,	*Polysaccharoses*, $(C_6H_{10}O_5)_n$,
+ Arabinose	+ Cane-sugar, or Sucrose	+ Starch
+ Ribose	+ Milk-sugar, or Lactose	+ Cellulose
+ Xylose	+ Malt-sugar, or Maltose	− Inulin
Hexoses, $C_6H_{12}O_6$.	*Trisaccharose*, $C_{18}H_{32}O_{16}$,	+ Glycogen
+ Glucose, Grape-sugar, or Dextrose	+ Raffinose, or Melitriose	+ Dextrin
− Fructose, Fruit-sugar, or Lævulose		The Gums
+ Galactose		
+ Mannose		

Properties of the carbohydrates.—Most of the natural carbohydrates are optically active in solution (p. 171); and in the table, the character of the rotation, whether dextro (right-handed) or lævo (left-handed), is indicated by the plus or minus sign.

Glucose, grape-sugar, or **dextrose,** is widely distributed among plants, especially in the sweet-tasting parts, as in the nectar of flowers and in ripe fruit, where it is usually associated with fruit and cane-sugar. It has received the name grape-sugar from its presence in ripe grapes, of dextrose from its dextro-rotation, and of glucose from its sweet taste (γλυκύς, sweet).

The discovery of a lævo-rotatory grape-sugar has led to the substitution of the name **dextro-glucose,** or simply glucose, for dextrose, although the latter name is still retained for the natural sugar. Glucose is a constituent of many glucosides (p. 209). In cases of *diabetes mellitus* it is found in the urine, sometimes to the extent of 8 to 10 per cent.

In small quantities pure glucose is most readily obtained from cane-sugar. Cane-sugar is dissolved in 90 per cent. alcohol and a little strong hydrochloric acid added. On gently warming the mixture, the cane-sugar is hydrolysed and breaks up into glucose and fructose:

$$\underset{\text{Cane-sugar.}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Glucose.}}{C_6H_{12}O_6} + \underset{\text{Fructose.}}{C_6H_{12}O_6}.$$

Glucose, being less soluble in alcohol than fructose, separates in anhydrous crystals.

EXPT. 73.—**Preparation of Grape-sugar.**—Mix together 300 c.c. of alcohol (strong spirit will do) and 12 c.c. concentrated hydrochloric acid and warm to 45°–50° and add gradually 100 grams of cane-sugar and stir until dissolved. Add a few crystals of anhydrous grape-sugar and allow the solution to stand for a day or two in as cold a situation as possible. Grape-sugar melts at 196°.

Glucose is manufactured by boiling starch with very dilute sulphuric acid. The starch is thereby hydrolysed and converted into glucose (p. 163). The resulting liquid is neutralised with chalk and filtered, and the filtrate decolorised by filtration through animal

charcoal. The solution is evaporated to the requisite consistency in vacuum-pans (p. 156). The product solidifies on cooling, and forms an amorphous-looking mass, which always contains dextrin (p. 164). Commercial glucose is used as a sweetening material in the manufacture of confectionery, preserved fruit and jam, wines, liqueurs, and as a substitute for malt in the brewing of beer.

Properties of glucose.—Pure glucose dissolves in 1·2 parts of water. It crystallises from aqueous solution with 1 molecule of water, and the crystals melt at 86°, whilst from alcohol the anhydrous compound separates, melting at 146°. Glucose is dextro-rotatory in aqueous solution. Its **specific rotation**[1] is given by the expression $[\alpha]_D = +52°{\cdot}5$.

Reactions of glucose.—Glucose gives the following series of reactions: Caustic alkalis, added to a solution of glucose and warmed, produce a brown solution.

EXPT. 74.—Add a few drops of caustic soda solution to a dilute solution of glucose, and warm gently. The colour of the liquid changes to yellow and then to brown.

Glucose reduces an ammoniacal solution of silver nitrate, metallic silver being deposited.

EXPT. 75.—Add a few drops of a solution of glucose to half a test-tube of ammonia silver-nitrate solution, and heat the test-tube in hot water. A mirror of silver will be deposited.

An alkaline solution of copper sulphate is reduced, and cuprous oxide is precipitated.

EXPT. 76.—Add two or three drops of copper sulphate solution to a solution of glucose, and then caustic soda solution, until a

[1] The term **specific rotation** is used to denote the deviation of polarised light produced by a liquid or solution containing 1 gram of substance in 1 c.c. of liquid in a layer 1 decimetre in length. This is calculated from the strength of the solution and the length of the column of liquid with which the deviation is determined; the deviation being proportional to the strength of the solution and the length of the column of liquid. The specific rotation is represented by the symbol $[\alpha]_D$, the D standing for monochromatic light produced by the sodium flame. The temperature should also be indicated by writing it above the letter D, thus, $[\alpha]_D^{20°}$.

clear blue solution is obtained. When the liquid is boiled a yellow precipitate of cuprous oxide is formed, which rapidly turns red.

The following reaction, which is given by all soluble carbohydrates, is known as **Molisch's test.**

EXPT. 77.—Add two or three drops of an alcoholic solution of α-naphthol to the glucose solution and carefully pour down the side of the test-tube some strong sulphuric acid. At the junction of the two layers a blue or violet colour will be developed.

Phenylhydrazine in presence of acetic acid produces, on heating, a yellow, crystalline precipitate of phenylglucosazone.

EXPT. 78.—Dissolve about 0·5 gram of glucose in 5 c.c. of water, and add a solution of phenylhydrazine acetate. The acetate is prepared by dissolving about 1 gram of phenylhydrazine in the same weight of glacial acetic acid and diluting to 10 c.c. Mix the two solutions in a test-tube and heat in boiling water. In a few minutes a yellow, crystalline mass of phenylglucosazone is deposited, seen under the microscope in the form of crystalline tufts. The substance melts at 204°–205°. The reaction occurs according to the following series of equations. Glucose phenylhydrazone is first formed:

1. $CH_2.OH$ — $(CH.OH)_4$ — $CH{:}O + H_2N.NH.C_6H_5$ $= CH_2.OH$ — $(CH.OH)_4$ — $CH{:}N.NH.C_6H_5 + H_2O.$

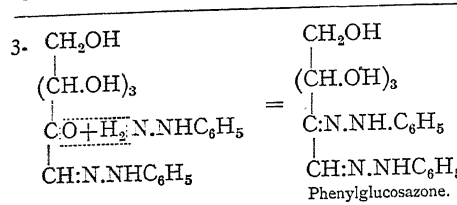
Glucose phenylhydrazone.

The glucose phenylhydrazone is oxidised by a second molecule of phenylhydrazine and converted into a ketone, which is the phenylhydrazone of glucosone, and the latter unites with a third molecule of phenylhydrazine and forms the glucosazone:

2. $CH_2.OH$ — $(CH.OH)_3$ — $CH.OH$ — $CH{:}N.NH.C_6H_5 + NH_2.NH.C_6H_5 =$ $CH_2.OH$ — $(CH.OH)_3$ — CO — $CH{:}N.NHC_6H_5 + NH_3 + NH_2C_6H_5.$

Aniline.

Phenylhydrazone of glucosone.



Phenylglucosazone.

Constitution of glucose.—Glucose forms a pentacetyl derivative, and therefore contains 5 hydroxyl groups. Each hydroxyl group is probably attached to a different carbon atom, seeing that when 2 hydroxyl groups are attached to the same carbon atom the elements of water are removed. On oxidation it gives **gluconic acid**, $C_5H_{11}O_5CO_2H$, and **saccharic acid**, $C_4H_8O_4(CO_2H)_2$. The various reactions already described stamp glucose as an aldehyde. The formula for glucose is therefore that of a pentahydroxyaldehyde:

$$CH_2(OH).CH(OH).CH(OH).CH(OH).CH(OH).CHO.$$

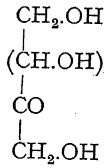
Structural formula for Glucose.

Fructose, fruit-sugar, or **lævulose,** $C_6H_{12}O_6$.—It has already been stated that fruit-sugar is associated with grape-sugar in many fruits, and the mixture is probably produced by the hydrolysis of cane-sugar, which is now known to precede the formation of the other carbohydrates in plants. The name *lævulose*, which was given to the natural sugar on account of its lævo-rotation, has been replaced by the word *fructose*, since the discovery of a dextro-rotatory fruit-sugar. Fructose may be obtained from cane-sugar by hydrolysis with dilute sulphuric acid, but is prepared commercially by the hydrolysis of inulin (p. 167).

Fructose is now produced commercially for the use of diabetic patients to replace cane-sugar. It appears to be assimilated, whereas glucose is excreted unchanged. Fructose crystallises in rhombic prisms which melt at 95°. It is lævo-rotatory, $[\alpha]_D^{20°} = -92°$. It has a sweet taste and gives many of the reactions of glucose. Although fructose is not an aldehyde but a ketone (see below), it nevertheless reduces alkaline copper solution. This is due to the presence of the easily oxidisable group —CO.CH_2(OH). With phenylhydrazine, fructose yields an osazone, which is identical with glucosazone. Fructose also undergoes fermentation with yeast, though less readily than

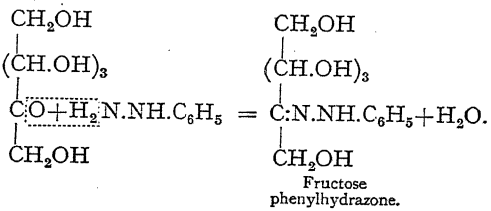
glucose, the latter being first removed when a solution of the two sugars is fermented.

Constitution of fructose.—Fructose forms a pentacetyl derivative, like glucose. On oxidation, it does not, like glucose, form an acid with the same number of carbon atoms, but breaks up into formic acid and trihydroxybutyric acid. This decomposition points to the presence of a ketone group in the molecule :

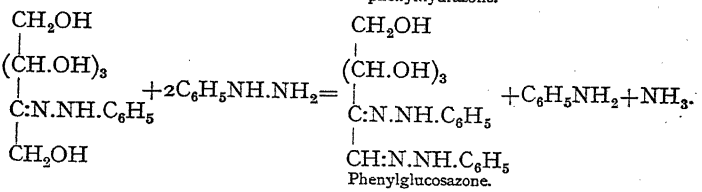


Fructose.

The above formula for fructose agrees, moreover, with the production of the same osazone as that obtained from glucose, a reaction in which the two end carbon atoms of the chain are involved (p. 152) :



Fructose phenylhydrazone.



Phenylglucosazone.

Galactose, $C_6H_{12}O_6$, is obtained from milk-sugar, or lactose (p. 160), by boiling with dilute sulphuric acid. The milk-sugar decomposes into glucose and galactose in much the same way that cane-sugar yields glucose and fructose :

$$\underset{\text{Milk-sugar.}}{C_{12}H_{22}O_{11}}+H_2O=\underset{\text{Glucose.}}{C_6H_{12}O_6}+\underset{\text{Galactose.}}{C_6H_{12}O_6}.$$

Galactose is less soluble in water than glucose or fructose. It crystallises in microscopic, hexagonal plates melting at 68°.

It forms a pentacetyl derivative. On reduction it yields **dulcitol** and on oxidation it forms the monobasic acid, **galactonic acid**, which is isomeric with gluconic acid, and the dibasic acid, **mucic acid**, which is isomeric with saccharic acid. It reduces alkaline copper sulphate solution, forms an osazone, which melts at 193°–194°, and undergoes fermentation by yeast, but more slowly than either glucose or fructose. The properties of galactose point to the same structural formula as that of glucose, and the difference between the two compounds must be one of space arrangement or configuration of the atoms (p. 173). It is dextro-rotatory, $\alpha_D = +80°$.

Mannose, $C_6H_{12}O_6$, was first obtained by the oxidation of mannitol with bromine in presence of sodium carbonate; but it has since been identified as one of the products of hydrolysis of certain carbohydrates, such as the cellular tissue of the **ivory-nut**. Mannose, unlike the other hexoses, forms an insoluble phenylhydrazone by which it may be identified. It has the same structural formula as glucose, and yields the same osazone, but possesses a different configuration. It is dextro-rotatory, and undergoes fermentation by yeast.

Disaccharoses

Cane-sugar, $C_{12}H_{22}O_{11}$, is found in the root, the tubers, and in the stems and flowers of many plants, as well as in the sap of certain trees. It is obtained chiefly from beet-root and sugar-cane; and in the United States, to a small extent, from the sugar maple, maize, and sorghum, a plant belonging to the grass family. Cane-sugar, known as **jaggery**, is made from a species of palm.

The sugar-cane was originally grown in the East—India and Arabia—and was introduced into Southern Europe by the Moors, whence it was transplanted to the West Indies and other tropical countries.

The sugar-cane industry.—The sugar-cane contains 16–18 per cent. of cane-sugar. The canes are cut up and passed between hot rollers, whereby the juice is expressed. The extracted canes are known as **begasse**. The juice, which contains 19–20 per cent. of sugar, and small quantities of inorganic salts, organic acids, and protein substances (p. 235), is run directly

into a copper vessel or **clarifier**, mixed with milk of lime, and boiled. The proteins are coagulated, and, together with the lime salts of the acids, form on the surface a scum which is removed. The juice is further concentrated until the point of crystallisation is reached, when it is run into casks, the bottoms of which are pierced with holes through which the molasses, or treacle, drains, or the crystals are separated by a centrifugal machine. The raw, or Muscovado, sugar is exported, and subsequently undergoes a process of refining, which is described later.

The beet-root sugar industry.—The presence of sugar in beet-root was observed in 1747 by the German chemist Marggraf, who suggested the cultivation of beet as a source of sugar; but the early attempts to utilise it commercially proved unprofitable. The success of the industry dates from about the year 1830, when important improvements began to be introduced. Careful selection of seed, and improved cultivation, nearly doubled the quantity of sugar in the beet. The use of steam-heated vacuum-pans gave a larger yield of crystallisable sugar, and new mechanical appliances for saving labour lowered the cost of production. Moreover, a method for revivifying the charcoal used for decolorising the raw sugar (after being used for a time it becomes inactive), and the introduction of a process for separating crystallised sugar from the molasses, combined to cheapen the product.

Beet-root contains about 13–14 per cent. of cane-sugar. The other solid constituents are a sugar known as **raffinose** (p. 161), which subsequently remains in the molasses, small quantities of citric, oxalic, tannic, and tartaric acids, protein, asparagine (p. 234), etc. The roots are washed and rasped into very thin slices, and then macerated in warm water. The process of maceration is known as **diffusion.** It is in reality a process of dialysis, the cell-wall acting as a diaphragm through which the sugar and the other crystalline substances pass, whilst the protein and non-crystalline contents of the cell are retained. The maceration is conducted in a series, or **battery** of tanks containing the beet-root pulp, and filled up with hot water. The pulp in each tank is in a different stage of extraction, fresh

pulp being at one end of the series and extracted pulp at the other. The water is pumped through the tanks in succession, so that fresh water comes in contact with the exhausted pulp, whilst the highly charged juice, which has passed through the tanks, is used for extracting the fresh beet. The juice, drawn from the tanks, is then heated with the addition of lime, which precipitates the acids and coagulates the protein. Carbon dioxide is passed through the liquid to decompose the saccharosate of lime which is formed. The two processes, which are usually combined in one operation, are termed respectively **defecation** and **saturation.** The operation is sometimes repeated, using sulphur dioxide in place of carbon dioxide to decolorise the juice. The mixture is now pumped through a filter-press to remove the insoluble substances, and the clear juice is evaporated in vacuum-pans, heated by steam from which the air is partially exhausted. A form of vacuum-pan is shown in section in Fig. 45. It consists of an iron pan, which is heated by vertical steam coils placed in the lower part of the vessel. Two or three pans are connected, so that the steam arising from the evaporation of the liquid in the first pan is utilised for heating the next, and its vapour passes on to the third. Between the pans a small cylindrical vessel is interposed, which serves to collect any juice which "primes," or is carried over during the boiling. The evaporation is continued until the liquid is so far concentrated

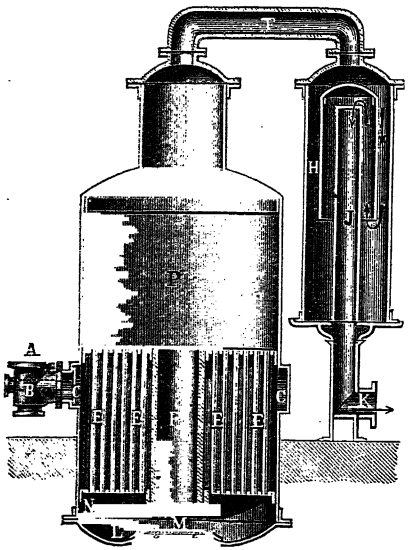


FIG. 45.—Vacuum-pan.

that it shows "grain," or commences to crystallise. It is then run out and cooled, and the uncrystallisable portion, or molasses, separated in a centrifugal extractor.

Extraction of sugar from molasses.—The foreign substances in the molasses prevent its crystallisation. Among the numerous processes proposed for separating crystallisable sugar from molasses, the **strontia method** is most commonly used. By this method nearly the whole of the cane-sugar is separated in the crystalline form. A hot saturated solution of strontium hydrate is added to the molasses, which, when excess of strontia is present, causes the separation of saccharosate of strontium, $C_{12}H_{22}O_{11}.SrO$. The latter is removed by filtration, dissolved in water, and decomposed by carbon dioxide, which precipitates strontium carbonate. The filtered liquid is evaporated, and the sugar crystallises. The syrup, which contains uncrystallisable sugar, is fermented and yields alcohol on distillation. By evaporation and destructive distillation of the dry residues, potash salts remain, some methyl alcohol distils, whilst methylamines (p. 205), ammonia and hydrocyanic acid are recovered from the gases.

Sugar refining.—Raw sugar from the cane as well as from beet-root has a brown or yellow colour, and requires refining, which is usually carried on in separate factories. The raw sugar is dissolved in water, and the solution heated with lime and occasionally with other substances. It is then filtered and the clarified juice passed through charcoal filters. These filters consist of long cylindrical vessels filled with animal charcoal, through which the saccharine liquid percolates and is decolorised. The juice is again concentrated in vacuum-pans and crystallised. The charcoal is revivified by washing, drying and finally heating in closed vessels.

EXPT. 79.—Take a long wide tube open at the top and fitted at the lower end with cork and glass tap. Fill the tube with fragments of animal charcoal and allow a solution of caramel (see p. 158) in water to trickle through. The liquid which runs out at the bottom will be colourless.

The annual production of beet-root sugar in Europe is about one-half of the total production of the world, which is estimated at about 16 million tons. All European countries produce

beet-root sugar except Great Britain, although it has the largest consumption ($2\frac{1}{2}$ million tons or 83 lb. per head per annum). A certain amount is also produced in the United States.

Sugar analysis.—Cane-sugar is optically active and turns the plane of polarisation to the right, $[\alpha]_D = +66°{\cdot}5$. The most accurate method for estimating the amount of sugar present in a commercial sample is to measure the rotation by means of a polarimeter (p. 171), which, when applied for this purpose, is usually termed a **saccharimeter.** Another method of analysis is to determine the refractive index of the solution by means of a **refractometer.**

Properties of cane-sugar.—Cane-sugar crystallises from aqueous solution in monoclinic prisms which melt at 160°–161°. When allowed to deposit slowly on threads suspended in the solution, large crystals known as **sugar candy** are formed.

Cane-sugar, like glycerol, glucose and certain other hydroxy-compounds, has antiseptic properties, and prevents the decay of putrescible matter. The sugar in candied fruits and jam acts as a preservative.

When cane-sugar is heated with a little water until it melts and begins to turn yellow, it forms, on cooling, a hard, glassy mass, which is called **barley-sugar.** If sugar is heated above its melting-point, it turns brown and forms **caramel,** a semi-solid, amorphous substance which is used in confectionery and for tinting spirits.

When sugar is heated in a retort, water, acetic acid, acetone and other products distil, and a very pure form of charcoal known as **sugar charcoal** is left.

Dilute sulphuric acid hydrolyses cane-sugar and converts it into equal proportions of glucose and fructose (p. 149). The mixture is known as **invert-sugar,** and the process as **inversion.** The name has originated from the change of sign in the rotation. Whereas cane-sugar is dextro-rotatory, when a mixture of equal quantities of the two hexoses is present, the lævo-rotation of fructose, $[\alpha]_D = -92°$, more than neutralises the dextro-rotation of glucose, $[\alpha]_D = +52{\cdot}5°$, and consequently the effect is lævo-rotatory.

Strong sulphuric acid gradually decomposes and chars cane-

sugar. The action is much more rapid if a little water is first added to the sugar. The charred mass then froths up and evolves carbon dioxide and sulphur dioxide.

Strong hydrochloric acid decomposes cane-sugar like the hexoses. Strong nitric acid oxidises cane-sugar and forms oxalic acid (p. 178).

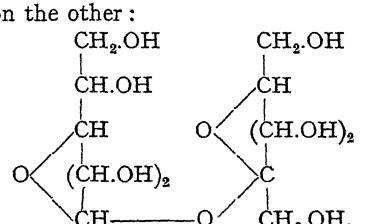
Cane-sugar forms saccharosates or sucrosates of the metals. It combines with 1, 2, and 3 molecules of strontia. The compound with one molecule of strontia has already been mentioned in connection with the recovery of sugar from molasses.

Cane-sugar is not directly fermentable by yeast. Before fermentation takes place the sugar undergoes inversion by means of the enzyme, invertase (p. 148). It has no reducing action upon an alkaline copper solution until it has been hydrolysed.

EXPT. 80.—Make a solution of cane-sugar and divide it into two portions ; boil one portion with a drop or two of dilute sulphuric acid. Add to each two drops of copper sulphate solution, and then caustic soda solution, until a clear blue solution is obtained. On boiling, cuprous oxide is precipitated by the hydrolysed sugar, but not by the unchanged cane-sugar.

It would appear from this indifference to alkaline copper solution that cane-sugar is not an aldehyde, and this view is confirmed by its behaviour with phenylhydrazine, with which it does not combine.

Constitution of cane-sugar.—Cane-sugar is clearly a compound of glucose and fructose. The absence of the properties of aldehydes and ketones renders it probable that the union of the two hexoses is in the nature of an anhydride or ether, formed by the linking of the aldehyde group of the one molecule to the ketone group on the other :



Probable structure of Cane-sugar.

Milk-sugar, lactose, $C_{12}H_{22}O_{11}+H_2O$, is present in the milk of mammals. An average sample of cows' milk has the following composition:

Water	86·8	per cent.
Milk-sugar	4·8	,,
Fat (butter)	3·6	,,
Casein and soluble protein	4·0	,,
Mineral matter (calcium phosphate, etc.)	0·7	,,
	99·9	

The milk-sugar is separated by coagulating the protein of the milk with **rennet**, or by the addition of a little acetic acid. The liquid is filtered and evaporated. The residue is milk-sugar. The whey which is obtained as a by-product in the manufacture of cheese is used as a source of milk-sugar. Milk-sugar forms large, hard crystals containing one molecule of water of crystallisation, which it loses at 130°. It is strongly dextro-rotatory, $[\alpha]_D^{20°} = +52°{\cdot}5$. It reduces alkaline silver and copper solutions, and forms an osazone of melting-point 200°. Milk-sugar is coloured yellow with alkalis. It is not directly fermentable with ordinary yeast, but certain bacteria readily convert it into lactic (p. 170) and butyric acids (p. 117). A ferment, or fungus, consisting of yellow nodules known as **kephir grains**, and containing bacilli and yeast, has the property of fermenting cows' milk and converting the milk-sugar into alcohol and carbon dioxide. **Koumiss** is a Russian beverage, and is made in a similar way by fermenting mares' milk. Milk-sugar yields glucose and galactose on hydrolysis (p. 153).

Maltose, malt-sugar, $C_{12}H_{22}O_{11} + H_2O$.—Maltose is produced by the action of diastase on starch. It is the sugar which is formed in the brewing of beer or manufacture of whisky, when the malted grain is steeped in water, which is ultimately fermented and converted into alcohol (p. 23). Maltose is readily prepared in the following way: an extract of malt is made by steeping the crushed grain in water for 24 hours and adding a little of the solution, which contains diastase, to starch-paste, and heating to a temperature of 60°–65° for an hour. The paste, which has by this time become liquid, is boiled and filtered, and evaporated on the water-bath until the liquid becomes syrupy. It is then extracted with 90 per cent. alcohol, which

removes the maltose. The extract is concentrated to a syrup by evaporation, and a crystal of maltose added, which induces the crystallisation of the mass. Maltose crystallises in fine needles. It is strongly dextro-rotatory, $[\alpha]_D = +140°{\cdot}6$. It reduces alkaline copper solution, and forms, with phenylhydrazine, maltosazone melting at 206°, which has a characteristic crystalline appearance under the microscope. On boiling with dilute sulphuric acid, maltose is hydrolysed, and is converted into glucose:

$$\underset{\text{Maltose.}}{C_{12}H_{22}O_{11}} + H_2O = 2\underset{\text{Glucose.}}{C_6H_{12}O_6}.$$

Maltose undergoes fermentation by yeast, the sugar being probably first hydrolysed into glucose by the action of an enzyme, **maltase**, which is contained within the yeast cell. It seems, in fact, definitely proved that only the simple hexoses are directly fermentable, and that the disaccharoses are all hydrolysed before conversion into alcohol and carbon dioxide can take place.

Raffinose, melitriose, $C_{18}H_{32}O_{16} + 5H_2O$, is obtained from beet-root molasses, and from other sources. It is strongly dextro-rotatory, $[\alpha]_D = +104°$. It decomposes, on hydrolysis, into glucose, fructose, and galactose.

Polysaccharoses

Starch, $(C_6H_{10}O_5)_n$, is found in various parts of plants, especially in the seeds and tubers, where it is stored as a reserve material to serve as nutriment for the young plant. The chief sources of starch are the potato, rice, maize, and wheat, which contain the following average percentages of starch:

Potato	15–20 per cent.
Wheat, and other cereals	60–65 ,,
Maize	65 ,,
Rice	75–80 ,,

Arrow-root starch is obtained from the tubers of certain species of maranta, a plant which grows in the tropics; **sago** is derived from the pith of the sago-palm; and **tapioca** is prepared from the tubers of manihot or cassava. In the case of **sago,** the starch is moistened and pressed through a sieve, the grains being rounded and hardened by being rubbed together and heated on hot metal plates. Sometimes potato starch is given the form of sago or tapioca.

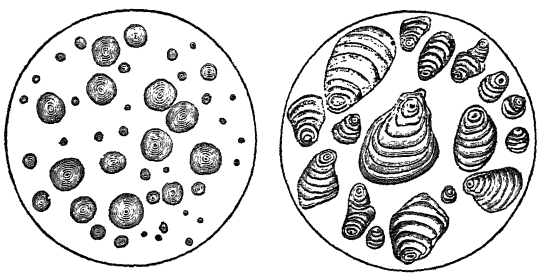
Manufacture of starch.—In England, starch is prepared chiefly from rice, whilst potatoes are employed in Germany, and maize, or Indian corn, in the United States. The process of manufacture is mainly mechanical. The material is softened and crushed, and then washed by a stream of water through revolving cylinders covered with fine wire or silk, which act as sieves, allowing the starch granules to pass, but retaining the gluten, or vegetable protein and cellulose, or cell-wall. The starch is further washed on sloping troughs to remove the lighter fibrous particles, and is then drained in a centrifugal extractor and dried. Rice, maize, and wheat, in which the starch is firmly cemented to the gluten of the grain, is disintegrated before washing, either by fermentation or by the action of dilute caustic soda, which dissolves the protein.

EXPT. 81.—Enclose a handful of flour in a small muslin bag and knead it under water. The starch grains pass through the meshes of the muslin into the water and produce a milky liquid, whilst the gluten remains in the bag as a tough, sticky mass. Examine some of the milky fluid under a good microscope, and notice the appearance of the grains.

Properties of starch.—The appearance of different kinds of starch under the microscope is characteristic. The grains may be round, elliptical, or angular, and of different sizes. In Fig. 46 is shown the microscopic appearance of wheat and potato starch of the same magnification.

The grains consist of concentric rings, or layers, arranged round a nucleus. Between crossed Nicols they present the appearance of a doubly refracting crystal. Starch is insoluble in cold water, but, when heated, the granules swell up and burst, forming a slightly opalescent solution, which on cooling sets to a stiff paste known as **starch-paste.** The soluble portion is termed **granulose,** and the insoluble part which renders the liquid turbid is known as **starch cellulose.** When starch is heated with water under pressure, with glycerol, or with dilute acids, it dissolves in hot water, and separates on cooling in the form of an amorphous white powder. It is known as **soluble starch.** The molecular weight of soluble starch has been determined by the freezing-point method (p. 17), and found to correspond with the formula

$C_{1200}H_{2000}O_{1000}$. When starch is heated below a point at which it becomes discoloured, it is converted into **dextrin** (p. 164). The most characteristic reaction for starch is its behaviour with iodine. A solution of starch-paste in water is coloured blue by free iodine. The colour disappears on warming, but returns when the liquid cools. The reaction is very delicate, 0·003 milligram of iodine being detected in this way. It has already been stated that when extract of malt, in water or diastase solution, is added to starch paste, and the mixture maintained at a temperature of about 60°, the starch soon liquefies and becomes limpid. If iodine solution is added at intervals to



Wheat starch (highly magnified). Potato starch (highly magnified).

FIG. 46.

portions of the solution from the moment liquefaction occurs, the following appearances will be observed: a blue solution is first obtained; this is the ordinary reaction for starch or soluble starch; the coloration of succeeding portions is purple, then red, until, finally, no coloration is produced. These changes are caused by the disintegration of the starch molecule into simpler compounds known as **dextrins**, the latter being ultimately decomposed and converted into maltose (p. 160), when the action ceases. Saliva and pancreatic juice, which contain hydrolytic enzymes (ptyalin) resembling diastase, produce a similar effect on starch. An analogous series of changes is brought about by boiling starch with dilute sulphuric acid, but as the maltose is also hydrolysed, the starch is almost completely converted into glucose (p. 149).

EXPT. 82.—Make a thin solution of starch paste by grinding up about 2 grams with a little cold water and pouring the mixture into 50 c.c. of boiling water. Divide the solution into three parts. Add a few c.c. of malt extract to one portion, and warm to 60°; add a little saliva to another; and boil a third portion with a few drops of dilute sulphuric acid. Test a portion of each both with iodine solution and alkaline copper solution from time to time. In each case the blue colour will gradually give place to violet, then red, and finally the colour will disappear, whilst the presence of maltose or glucose will be indicated by the precipitation of cuprous oxide with Fehling's solution.

Uses of starch.—Starch is used for sizing and stiffening paper and cloth, for laundry purposes and for the manufacture of dextrin or British gum.

Dextrin, $(C_6H_{10}O_5)_n$, is obtained from starch by the action of a gentle heat or by partial hydrolysis with diastase or dilute sulphuric acid. It is usually manufactured by moistening starch with a mixture of dilute nitric and hydrochloric acid, and heating to 100°–125°. It forms a yellowish powder with a peculiar smell, which dissolves in water, forming a clear mucilage. It is employed under the name of **British gum.**

Cellulose, $(C_6H_{10}O_5)_n$, is a fundamental constituent of the cell-walls of plants, and forms the framework, or skeleton, of vegetable tissues. It is probably elaborated from simpler carbohydrates secreted by the protoplasm of the cell. Cellulose in a pure state is best known to us as cotton-wool, linen, and paper. The difference between cotton and linen is due rather to the structure of the fibres, which consist of cylindrical tubes, than to the chemical nature of the substance composing them. Both kinds of fibre contain a small quantity of mineral matter, which is left as ash on burning the organic matter. The mineral matter is almost entirely removed by the action of hydrofluoric acid. The best filter papers are prepared by treatment with this acid, after which they are well washed with water, alcohol, and ether. These papers, which are sometimes known as Swedish filter papers, consist of cellulose in its purest form. A careful study of the cellular tissues has shown that cellulose does not represent one only, but several substances, which may be differentiated by the products which they yield on

hydrolysis. Some, like cotton and linen, give glucose; others mannose; and others, again, galactose and the pentoses, xylose and arabinose (p. 168).

Properties of cellulose.—We are most familiar with the chemistry of the cellulose of cotton fibre. It is an unusually inert substance compared with the other carbohydrates. It is scarcely affected by chlorine, or bromine, or by boiling dilute acids or alkalis. These reagents are consequently employed in separating the fibre from encrusting matter, resin, gum, and wax, with which it is usually associated. In the manufacture of paper and in the cleaning and bleaching of cotton, both caustic soda and hypochlorites are used. It is this inertness towards the common reagents which renders paper so serviceable as a filtering medium.

A strong solution of caustic alkalis produces a curious thickening and gelatinising of the walls of the fibre, which causes the cellulose to shrink and become translucent. The effect of pouring a strong solution of caustic soda on to filter paper is very marked. It rapidly thickens and contracts. When applied to cotton fibre and cloth the process is named **mercerising**, after its discoverer, and is used for producing crinkled surfaces on cotton fabrics. Strong sulphuric acid rapidly attacks and dissolves cellulose. If the sulphuric acid is diluted with water in the proportion of 2 volumes of sulphuric acid to 1 volume of water, and a piece of filter paper dipped into the liquid, the paper becomes immediately tough and translucent. When freed from acid and dried, it is known as **parchment paper.** Prolonged boiling with dilute sulphuric acid gradually breaks up the cellulose molecule and produces glucose. The decomposition is hastened by dissolving cellulose in very concentrated hydrochloric acid, and then diluting with water. Zinc chloride in hydrochloric acid dissolves cellulose, and so also does a solution of cupric oxide in ammonia, known as Schweizer's reagent. The latter solution is prepared by precipitating copper sulphate with caustic soda in the cold, washing the precipitate, and dissolving it whilst still moist in a little strong ammonia solution. Cotton-wool rapidly gelatinises in the solution and ultimately dissolves. The cellulose is thrown down from the solution by

the addition of acids, alcohol, or even common salt, in the form of a gelatinous precipitate resembling alumina. This reaction is utilised for producing artificial silk (p. 167) and also for preparing **Willesden paper.** The surface of the paper is moistened with the ammoniacal cupric oxide, which gelatinises the surface fibres, and, after drying, renders the paper impervious to water. Cellulose is readily acted upon by strong nitric acid, or a mixture of nitric and sulphuric acid, and yields a series of cellulose nitrates, **pyroxylins** or **nitro-celluloses.** These substances are not nitro-compounds, seeing that they are hydrolysed by alkalis and the nitrogen removed as nitrate of the alkali. They must be regarded as nitric esters of cellulose. The most important of these compounds is gun-cotton.

Gun-cotton, cellulose hexanitrate, $[C_{12}H_{14}O_4(O.NO_2)_6]_n$.—Gun-cotton is prepared by steeping pure cotton-wool in a mixture of 3 parts of fuming nitric acid and 1 part of strong sulphuric acid for twenty-four hours at a temperature not exceeding 10°. It is then removed and carefully washed with water until free from acid. When dry, the cotton, though still preserving its fibrous texture, is much more inflammable and burns with remarkable rapidity. When compressed into cartridges and detonated, it forms a powerful explosive. Gun-cotton is insoluble in a mixture of alcohol and ether, but dissolves in acetone, forming a jelly. This solution is mixed with nitroglycerin in the preparation of cordite (p. 145). When gun-cotton is dissolved in nitroglycerin, it forms blasting gelatine (p. 145). The lower nitrates of cellulose (tetra- and penta-nitrates) are prepared by a modification of the above reaction and are used for various purposes.

Collodion is the solution of the lower nitrates in a mixture of alcohol and ether. On evaporation of the solvent a transparent film of considerable tenacity remains. It is used for producing **artificial silk** (Chardonnet's process). The solution, to which dilute sulphuric acid is added, is forced through a fine orifice into water, where it is at once coagulated and forms a fine, transparent thread of considerable toughness. The threads, when wound on a reel and twisted, produce a silky fibre, which is rendered non-explosive by denitration with ammonium sulphide.

Artificial silk is also prepared from the gelatinous mass obtained by dissolving cotton in Schweitzer's reagent (Pauly), and also from the viscous product (viscose) made by treating cellulose with a mixture of carbon disulphide and caustic alkali (Cross and Bevan). Cellulose acetate is used for the same purpose. In all cases the viscid, transparent liquid is squeezed through a fine aperture and subsequently rendered insoluble.

Celluloid, Xylonite, consists of the lower nitrates of cellulose. They are dissolved in acetone and camphor, and other substances added. The mixture forms a plastic mass, which can be worked up for a variety of purposes. It is, naturally, extremely inflammable.

Manufacture of Paper.—A great variety of materials is employed in the manufacture of paper, such as linen and cotton rags, esparto grass, straw, and wood. The material is first disintegrated by mechanical means. The fabrics are torn up and the straw and wood cut into small pieces. The materials are converted into pulp by boiling with caustic soda in closed boilers heated by steam under pressure. Wood-pulp is prepared by using a strong solution of calcium bisulphite in place of caustic alkalis. The pulp is run out, washed and bleached with bleaching liquor, and again washed. It is then ready to be made into paper.

Inulin, $(C_6H_{10}O_5)_n + H_2O$, is found in inula, dahlia tubers and in the tubers, bulbs, and roots of other plants, where it appears to take the place of starch. It is a white powder, which does not give a blue colour with iodine. On hydrolysis it yields fructose (p. 152).

Glycogen, $(C_6H_{10}O_5)_n$, is widely distributed in the animal kingdom, and is sometimes known as **animal starch.** It appears to play the part of a reserve material, for it quickly disappears when food is not taken. Glycogen is found in the liver and in small quantities in muscle. It is also found in certain fungi, and is very plentiful in molluscs. Oysters contain as much as 9 per cent. of glycogen. It is a white, amorphous powder, which dissolves in hot water, and is precipitated by alcohol. Iodine colours it brown. It is strongly dextro-rotatory. Submitted to the action of diastase, it yields dextrin, maltose, and glucose.

Gums are transparent, glassy, amorphous substances, which are exuded from plants. They form a mucilage with water, from which the gum is precipitated by alcohol. They do not reduce

Fehling's solution, but are hydrolysed by acids into monosaccharoses. The monosaccharoses are not necessarily hexoses. The two pentoses, **arabinose** and **xylose**, are obtained from certain gums. **Gum arabic** is an exudation from the bark of several species of acacia. It consists of the calcium and potassium salts of arabic acid. When hydrolysed with dilute sulphuric acid, it yields **arabinose**, $C_5H_{10}O_5$. **Wood gum** is widely distributed throughout the vegetable kingdom. It is extracted from the wood of various trees by digestion with caustic alkalis and precipitation by alcohol. It is a white powder, which, on hydrolysis, yields **xylose**, $C_5H_{10}O_5$. d-**Ribose** has been shown to be a constituent of the nucleic acid of cell nuclei.

EXPT. 83.—The presence of pentoses may be shown by their behaviour with a solution of phloroglucinol (p. 289) or orcinol in strong hydrochloric acid. A pine shaving, or gum arabic, on gently warming with the solution, turns a bright cherry-red with the former and violet with the latter reagent, showing the presence of a pentose in both cases.

QUESTIONS ON CHAPTER XIV

1. Describe the system of classification adopted in the case of the carbohydrates.

2. What are the chief reactions of the monosaccharoses? Which of the disaccharoses give similar reactions?

3. Describe the preparation of glucose and fructose from cane-sugar. How can the two sugars be distinguished? How is fructose obtained from glucose? Why are the names glucose and fructose used in preference to the older names of dextrose and lævulose?

4. Give the products of hydrolysis of the three principal disaccharoses. How is maltose prepared? How is it distinguished from glucose?

5. How are the following compounds inter-related: starch, dextrin, dextrose, mannitol, gluconic acid, and saccharic acid?

6. What is the experimental evidence for the conclusion that dextrose contains an aldehyde group and lævulose a ketone group? How does phenylhydrazine react with each of these sugars?

7. How can the hydrolysis of starch, cellulose, cane-sugar, inulin, and glycogen be effected? State the properties of their hydrolytic products.

8. To what class of bodies does glucose belong? Where does

it occur? From what sources is it made, and how can it be recognised?

9. By what properties and reactions would you distinguish a solution of cane-sugar from a solution of glucose?

10. How would you demonstrate the production of glucose from cane-sugar and starch respectively?

11. What effect is produced on starch by the action of (1) heat, (2) dilute sulphuric acid, (3) nitric acid?

12. What are the principal differences between starch and cellulose? What evidence exists as to the molecular weights of these substances?

13. What is the action of (1) nitric acid, (2) sulphuric acid, and (3) caustic soda, on cellulose?

14. How are the following prepared: *starch*, *British gum*, *gun-cotton*, *Willesden paper*, *celluloid*, *collodion*, and *cordite*?

15. Describe and explain the changes which starch undergoes when acted on by malt extract. How could these changes be demonstrated?

16. Classify the natural carbohydrates. Give any general methods for distinguishing these substances as a group.

17. How would you distinguish the following dissolved in water: (1) glucose, (2) invert-sugar, (3) cane-sugar, (4) maltose?

18. Discuss the changes which hydrolysis (by acids or enzymes) effects in starch. How would you identify the products?

CHAPTER XV

THE HYDROXY-, DIBASIC, AND UNSATURATED ACIDS

Glycollic acid, Hydroxyacetic acid, $CH_2(OH).CO_2H$, is the first member of the series. It is found in unripe grapes, and in the leaves of the Virginian creeper. It is most readily obtained by boiling potassium chloracetate with water. The liquid is evaporated and the glycollic acid extracted with acetone, in which it readily dissolves, leaving the potassium chloride undissolved:

$$CH_2Cl.CO.OK + H_2O = \underset{\text{Glycollic acid.}}{CH_2(OH).CO_2H} + KCl.$$

It is a colourless, crystalline substance, which melts at 80°.

Lactic acid, Ethylidene lactic acid, *α-Hydroxypropionic acid,* $CH_3.CH(OH).CO.OH$.—The α-hydroxy-acid, or ordinary lactic acid, is present in sour milk, from which it was first isolated by Scheele in 1780. It is produced in milk by the lactic fermentation of milk-sugar (p. 160). The ferment consists of chains of cells resembling the acetic ferment (p. 56). Lactic acid is more readily prepared from cane-sugar or starch, the operation being practically the same as that used in the preparation of butyric acid (p. 117); but the decomposition is arrested before the butyric fermentation sets in. Cane-sugar is dissolved in water, and a little tartaric acid is added together with zinc or calcium carbonate to neutralise the free lactic acid. The ferment is added in the form of decayed cheese and sour milk, and the mixture is kept at a temperature of 40°–50° for several days. Crystalline crusts of zinc or calcium lactate separate, and are removed and recrystallised. The acid is obtained by decomposing the salts with sulphuric acid and extracting with ether.

On evaporating the ether, the lactic acid remains as a colourless, viscid liquid which possesses a sour smell and taste. It is also obtained from α-chloro- or bromo-propionic acid by boiling with water (p. 118), and by the hydrolysis of acetaldehyde cyanhydrin (p. 52):

$$\begin{array}{l} CH_3 \\ | \\ CH.OH \\ | \\ CN \end{array} + 2H_2O = \begin{array}{l} CH_3 \\ | \\ CH.OH \\ | \\ CO_2H \end{array} + NH_3.$$

Acetaldehyde cyanhydrin. Lactic acid.

When pure, lactic acid melts at 18° and distils at 1 mm. pressure, unchanged. Boiled with dilute sulphuric acid, it decomposes into acetaldehyde and formic acid:

$$CH_3.CH(OH).CO.OH = CH_3.CHO + H.CO_2H.$$

The calcium and zinc salts of lactic acid readily crystallise from hot water and are characteristic of the acid.

Para-, or sarco-lactic acid, $CH_3.CH(OH).CO.OH$.—The acid is found in muscle, to which it imparts an acid reaction, and is consequently present in the juice of flesh. A convenient source of the acid is Liebig's extract of meat. The extract is dissolved in water, and the protein precipitated by alcohol The alcohol is then driven off, the liquid acidified, and the sarcolactic acid extracted with ether. It is *optically active*, turning the plane of polarisation to the right, and in this respect it differs from the sour milk acid, which is inactive. Moreover, the zinc salt of sarcolactic acid contains only two molecules of water of crystallisation, whilst the other contains three. In all other chemical properties the two acids appear to be identical.

Optical activity.—When light is passed through a Nicol prism, only rays vibrating in one plane are transmitted, and the light is said to be **polarised.** A polarimeter is an instrument containing two Nicol prisms, fixed at short distances apart. If we imagine rays passing through the first prism to vibrate in a vertical plane, then, by turning the second prism, so that rays can only traverse it in a horizontal plane, the light from the first is totally extinguished by the second prism. If the second prism

is rotated, more and more light is transmitted, until the planes of transmission coincide, when the field is fully illuminated.

Supposing the Nicol prisms to be crossed, as in the first case, so that the light after traversing the first prism is extinguished by the second prism, the introduction of a layer of the active acid will allow some light to pass. Sarcolactic acid has the property of turning the plane in which the polarised rays vibrate from the normal direction to the right hand (dextro-rotatory), so that some light now finds its way through the second Nicol prism. In the case of other substances a left-handed (lævo-rotatory) rotation is imparted. This will be more easily understood by reference to Fig. 47.

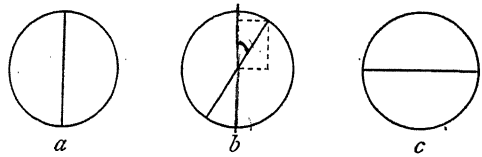


FIG. 47.

a represents the first Nicol prism and *c* the second, the plane of vibration being indicated by the cross lines. On introducing the acid, the plane of vibration of the polarised rays is twisted through a certain angle indicated at *b*. This new position may be regarded as the resultant of two forces, represented by vertical and horizontal components, indicated by dotted lines. The vertical component is extinguished when it reaches *c*, but the horizontal component passes through and produces a certain degree of illumination of the field of view. A greater twist will allow more light to pass, until the twist takes a horizontal position, when the maximum amount of light will be transmitted. The property of turning the plane of polarisation is also called **rotatory polarisation**, and is synonymous with optical activity. This property, possessed by certain liquids and solutions of solids, is found to bear a close connection with their structure. Optically active carbon compounds, without exception, contain within the molecule at least one carbon atom, united by its 4 bonds to 4 different elements or groups of atoms.

If we denote the carbon atom as a point from which 4 bonds diverge at equal angles (Fig. 48), and ABCD as 4 different

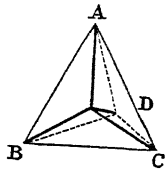
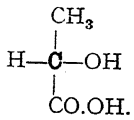


FIG. 48.

groups attached to these bonds, such a grouping is present in substances which, like sarcolactic acid, exhibit optical activity :



Sarcolactic acid.

In sarcolactic acid the central carbon atom is linked to the groups H, CH_3, OH, CO_2H. The central carbon atom is termed an **asymmetric carbon** atom. Represented by the space formula (Fig. 49) the arrangement is unsymmetrical in the sense that it cannot be divided in any direction into exactly similar halves.

But this formula is also that of the sour milk acid. How

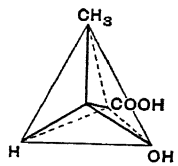


FIG. 49.

are we to bring these facts into harmony ? The explanation is based on the speculations of Pasteur (1860), further developed by van't Hoff and Le Bel (1874) into the present theory of space- or stereo-isomerism.

Theory of Space- or Stereo-isomerism.—Now every asymmetric or unsymmetrical object like a hand or foot has its fellow, but the two do not precisely overlap ; in the same way

every substance containing an asymmetric carbon atom, round which the four different groups are distributed in three-dimensional space, is capable of existing in two forms, which correspond to a left and right hand or to an object and its reflected image. The two forms will then appear as in Fig. 50. The one is the mirror-image of the other. .

When using actual models in which the different groups are represented by coloured sticks or balls, it will be found that the two models cannot be turned so as to coincide until two of the groups in one model have been interchanged. It has been shown that the only difference between two substances having a space arrangement of their atoms corresponding to object and image lies in their action on polarised light, the one turn-

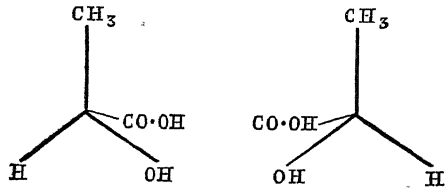


FIG. 50.—Stereo-isomeric forms of Lactic acid.

ing it to the right (dextro-rotatory) and the other the same amount to the left (lævo-rotatory) when in the dissolved or liquid state.

Although every optically active substance, like sarcolactic acid, contains at least one asymmetric carbon atom, the converse does not hold ; for there are compounds like sour milk lactic acid which possess an asymmetric carbon atom and show no rotation.

How is this explained ? The substance may be a mixture of equal quantities of the two forms, the dextro-rotation of the one form neutralising the lævo-rotation of the other.

This is the case with the sour milk acid. It has, in fact, been resolved into its two active components, a lævo- and a dextro-rotatory acid, the latter being identical with sarcolactic acid. The methods used for resolving inactive compounds into their active components will be referred to under tartaric acid (p. 190).

Hydracrylic acid, Ethylene lactic acid, *β-Hydroxypropionic acid,* $CH_2(OH).CH_2.CO.OH$.—This represents a third lactic acid, which, however, has a different structure from either of the previous acids. It is named hydracrylic acid from the fact of its losing a molecule of water on heating, and forming acrylic acid (p. 192). It is termed also ethylene lactic acid to denote that the acid contains the radical ethylene, $CH'_2.CH'_2$, thereby distinguishing it from ordinary lactic acid or ethylidene lactic acid, which contains the ethylidene radical, $CH_3.CH''$. The designation β-hydroxypropionic acid has already been explained (p. 118). Hydracrylic acid has been obtained synthetically by boiling the β-chloro- and bromo-propionic acids with water, or by acting upon ethylene chlorhydrin (p. 129) with potassium cyanide. The cyanhydrin, thus formed, yields the acid on hydrolysis. These changes are represented as follows:

$$\underset{\text{Ethylene chlorhydrin.}}{\begin{matrix}CH_2(OH)\\|\\CH_2Cl\end{matrix}} \xrightarrow{KCN} \underset{\text{Ethylene cyanhydrin.}}{\begin{matrix}CH_2(OH)\\|\\CH_2.CN\end{matrix}} \xrightarrow{H_2O} \underset{\text{Ethylene lactic acid.}}{\begin{matrix}CH_2(OH)\\|\\CH_2.CO.OH.\end{matrix}}$$

Hydracrylic acid is a thick, syrupy liquid resembling ordinary lactic acid.

The Aldehydic and Ketonic acids, as their name implies, combine the properties of aldehydes or ketones with those of acids.

Glyoxalic acid, Glyoxylic acid, $CHO.CO.OH + H_2O$, may be taken as the representative of an aldehydic acid. It is obtained by the oxidation of ethyl alcohol, glycol, or glycollic acid with nitric acid (p. 170), or by the reduction of oxalic acid on electrolysis or by means of magnesium powder.

EXPT. 84.—Place 10 grams of magnesium powder in a flask, cover with water and cool well in ice. Pour on 250 c.c. of a saturated solution of oxalic acid. After it has stood for a time, filter. The solution may be used for the test for proteins (p. 235). Add a little glacial acetic and strong sulphuric acid to a few drops of glyoxalic acid solution, and then a solution of egg-albumin; a violet coloration is produced.

Another method of preparing glyoxalic acid is to boil di(or dibrom-acetic acid with water. It will be observed when two hydroxyl groups are attached to the same ca atom, the elements of water are removed.

$$\underset{\text{Dichloracetic acid.}}{\begin{matrix}CHCl_2\\|\\CO_2H\end{matrix}} + 2H_2O = \underset{\text{Intermediate product.}}{\begin{matrix}CH(OH)_2\\|\\CO_2H\end{matrix}} + 2HCl = \underset{\text{Glyoxalic acid.}}{\begin{matrix}CHO\\|\\CO_2H\end{matrix}} + H_2O.$$

The acid is found in unripe fruits but disappears as the ripens. It appears to be formed in small quantities when a(acid is exposed to the air. Glyoxalic acid is usually obta as a syrupy liquid which slowly crystallises on standing. very soluble in water and volatilises in steam. Whilst it fo salts with bases, it also reduces ammoniacal silver solut producing a mirror, and combines with hydroxylamine phenylhydrazine like an aldehyde.

Pyruvic acid, $CH_3.CO.CO.OH$, is the simplest of the keto acids. It is most readily prepared by distilling tartaric a with acid potassium sulphate, which acts as a dehydrati agent:

$$\underset{\text{Tartaric acid.}}{C_4H_6O_6} = \underset{\text{Pyruvic acid.}}{C_3H_4O_3} + CO_2 + H_2O.$$

Pyruvic acid is a colourless liquid which boils at 165°. yields lactic acid on reduction, and acetic acid and carb(dioxide on oxidation:

$$\underset{\text{Lactic acid.}}{\begin{matrix}CH_3\\|\\CH(OH)\\|\\CO_2H\end{matrix}} \leftarrow \underset{\text{Pyruvic acid.}}{\begin{matrix}CH_3\\|\\CO\\|\\CO_2H\end{matrix}} \rightarrow \begin{matrix}CH_3\\|\\COOH\\+\\CO_2.\end{matrix}$$

The latter reaction occurs readily on warming with ammoni silver solution, the metal being deposited as a mirror. Th reduction of silver nitrate solution is therefore not limited t aldehydes alone, but is brought about both by ketonic alcohols like fructose (p. 152), and ketonic acids. The ketonic propertie of the acid are exhibited in the compound which it forms wit sodium bisulphite and the yellow, crystalline phenylhydrazone

which is precipitated on adding a solution of phenylhydrazine acetate to the acid.

Acetoacetic acid, $CH_3.CO.CH_2.CO_2H$, only exists in the form of its esters. Ethyl acetoacetate is formed by the action of sodium upon ethyl acetate.

The process is conducted as follows:—Metallic sodium, in thin slices, or as wire, is introduced into ten times its weight of pure ethyl acetate. The action, which begins slowly, becomes more vigorous after a time, and the liquid boils. The flask containing the mixture is then attached to an inverted condenser. To decompose the undissolved sodium, the liquid is finally heated on the water-bath. The sodium compound of ethyl acetoacetate is thus formed, from which dilute acetic acid liberates the ester as an oil, which floats on the surface of the liquid. The oil is removed and fractionated, the portion boiling at 175°–185° being separately collected. An alcoholic solution of ferric chloride gives a violet coloration.

THE DIBASIC ACIDS.

The Dibasic acids contain two carboxyl groups and consequently two replaceable hydrogen atoms. According to whether one or both hydrogen atoms are replaced, they form acid and neutral salts and esters—in some cases, salts with two different metals and salts containing a metal and an alkyl group. The dibasic acids may be regarded as paraffins in which two hydrogen atoms are substituted by carboxyl groups, or fatty acids in which one alkyl hydrogen is so replaced. Oxalic acid may be taken as representative of the group of dibasic acids. It forms the following series of compounds:

$\begin{matrix}CO.OH\\ \vert\\ CO.OH\end{matrix}$	$\begin{matrix}CO.OH\\ \vert\\ CO.OK\end{matrix}$	$\begin{matrix}CO.OK\\ \vert\\ CO.OK\end{matrix}$	$\left[\begin{matrix}CO.O\\ \vert\\ CO.O\end{matrix}\right]_2 Fe''(K_2)$
Oxalic acid, or Dicarboxyl.	Potassium hydrogen oxalate.	Potassium oxalate.	Potassium ferrous oxalate.

$\begin{matrix}CO.OH\\ \vert\\ CO.OC_2H_5\end{matrix}$	$\begin{matrix}CO.OC_2H_5\\ \vert\\ CO.OC_2H_5\end{matrix}$	$\begin{matrix}CO.OK\\ \vert\\ CO.OC_2H_5.\end{matrix}$
Ethyl oxalic acid.	Diethyl oxalate.	Ethyl potassium oxalate.

The dibasic acids are colourless, crystalline substances (with the exception of carbonic acid, which is known only in the form

of its salts and esters). They dissolve in water, to which impart a strongly acid reaction. The lower members cann distilled without decomposition.

Oxalic acid, $CO.OH.CO.OH + 2H_2O$.—Oxalic acid is in wood sorrel (*Oxalis acetosella*) and other plants, as the potassium salt. The salt is sometimes called **salts of s** The calcium salt is frequently found crystallised in plant Certain lichens growing on limestone consist largely of salt. It is also present in urine and in urinary calculi. produced by a peculiar fermentation of sugar caused by ce species of yeast and fungi. Scheele, in 1776, first obtained c acid artificially by heating sugar with nitric acid.

EXPT. 85.—**Preparation of Oxalic acid.**—Pour 180 c.c. of s nitric acid into a large flask (2 litres) and warm the acid on water-bath. Remove the flask to the fume cupboard and 50 grams of cane-sugar. Torrents of brown fumes are evo When the reaction has ceased, evaporate the liquid on water-bath to one-quarter its bulk. On cooling, large, co less, prismatic crystals of oxalic acid separate.

Oxalic acid is at present manufactured by heating so formate. It gives sodium oxalate, and hydrogen is evo (p. 75):

$$\begin{matrix} H.CO_2Na \\ H.CO_2Na \\ \text{Sodium formate.} \end{matrix} \rightarrow \begin{matrix} CO_2Na \\ | \\ CO_2Na \\ \text{Sodium oxalate.} \end{matrix} + H_2$$

EXPT. 86.—Heat a few grams of sodium formate in a test-t The gas which is evolved can be ignited at the mouth of the t If the residue is dissolved in water and filtered the solution g the reactions for oxalic acid (p. 179).

Oxalic acid is also obtained from pine sawdust, which is oxid by fusion with caustic alkalis. The sawdust is stirred into a paste with a mixture of strong caustic potash and soda solut and the paste is heated on iron plates. The temperatur gradually raised, care being taken to avoid charring. The brown mass is lixiviated with a small quantity of warm w which removes the excess of alkali and leaves the less sol sodium oxalate. The waste alkali is recovered and used ag

The sodium oxalate is dissolved in water and converted into the insoluble lime salt by boiling with milk of lime, and the lime salt is separated and decomposed with sulphuric acid. The liquid, separated from the calcium sulphate, is evaporated, when the oxalic acid crystallises in long prisms containing two molecules of water of crystallisation. There are various methods by which oxalic acid has been synthesised, some of which have already been mentioned. A solution of cyanogen in water changes into ammonium oxalate (p. 208).

Properties of Oxalic acid.—Oxalic acid crystallises in long, colourless prisms containing two molecules of water of crystallisation. When heated to 100°, the water of crystallisation is driven off. Above this temperature part of the acid melts, a part sublimes, and a certain amount decomposes into carbon dioxide and formic acid. When warmed with strong sulphuric acid, oxalic acid breaks up into carbon dioxide and carbon monoxide:

$$C_2O_4H_2 - H_2O = CO_2 + CO.$$

EXPT. 87.—Heat a few grams of oxalic acid, or an oxalate, with an equal bulk of strong sulphuric acid. Effervescence ensues without charring, and the gas which is evolved may be ignited.

Oxalic acid, in presence of dilute sulphuric acid, is rapidly oxidised by potassium permanganate, on warming, to carbon dioxide and water. The process is utilised in volumetric analysis:

$$5C_2O_4H_2 + 2KMnO_4 + 3H_2SO_4 = 10CO_2 + 8H_2O + K_2SO_4 + 2MnSO_4.$$

EXPT. 88.—Dissolve a few crystals of oxalic acid, or an oxalate, in water; add dilute sulphuric acid and warm gently. Add potassium permanganate, drop by drop. It is at first decolorised; but when the oxalic acid is all oxidised the pink colour remains.

Phosphorus pentachloride converts oxalic acid into **oxalyl chloride.** It is a colourless liquid which boils at 64°:

$$C_2H_2O_4 + 2PCl_5 = C_2O_2Cl_2 + 2POCl_3 + 2HCl.$$

Salts of Oxalic acid.—There are many important salts of oxalic acid. Potassium oxalate, $C_2O_4K_2 + H_2O$, is soluble in

water; the acid salt, C_2O_4HK, is less soluble and has been ferred to as a constituent of many plants. Acid potassium oxal combines with oxalic acid and forms what is known as potassiu quadroxalate, $C_2O_4HK.C_2H_2O_4+2H_2O$, which is sometimes us for removing ink-stains and iron-moulds, under the name **salts of sorrel**, or **salts of lemon**. The calcium salt, C_2O_4(is found in plants; the precipitated salt, which is thrown do when calcium chloride is added to a solution of an oxala contains one molecule of water of crystallisation. Ferr oxalate, $C_2O_4Fe+2H_2O$, is precipitated as an insoluble, yell powder when a ferrous salt is added to an oxalate in soluti Potassium ferrous oxalate, $(C_2O_4)_2K_2Fe+H_2O$, has strong ducing properties, and is used as a developer in photograp It is obtained by mixing solutions of ferrous sulphate and pota ium oxalate in certain proportions. The ferric alkali salts ha a green colour. The alkyl salts, or esters, of oxalic acid obtained by boiling the alcohol with anhydrous oxalic acid a distilling the product. **Methyl oxalate** is a solid, which melts 54° and boils at 162°; **ethyl oxalate** is a liquid boiling at 18 Both esters are rapidly hydrolysed by alkalis, in the cold.

EXPT. 89.—**Preparation of Methyl oxalate.**—Heat 70 grams crystallised and powdered oxalic acid in the air-bath at 110°-12 until it loses the weight corresponding to 2 molecules of wat The dehydrated and powdered acid is mixed with 63 c.c. of meth alcohol and heated for two hours on the water-bath with a refl condenser. The product is then distilled with a thermometer a when the temperature rises to 160° the receiver is changed and t water run out of the condenser. The distillate is methyl oxala which solidifies on cooling, m.-p. 54°. Add a little caustic pota to a little of the oxalate, dissolved in alcohol. Potassium oxal is deposited. To another portion of the solution add concentrat ammonia. A white, crystalline precipitate of oxamide is form (p. 124).

Malonic acid, $CH_2(CO.OH)_2$, is found as the calcium s in beetroot. It was originally prepared by the oxidation malic acid (p. 182) with potasssium dichromate and sulphu acid, a process which gave rise to the name; but it is now us to obtain it from monochloracetic acid. Potassium chloracet is boiled with potassium cyanide. The cyanacetate of potassiu

is then hydrolysed with strong hydrochloric acid; the product is evaporated to dryness and extracted with ether. When the ether has evaporated, malonic acid remains:

$$\begin{matrix}CH_2Cl\\|\\CO_2K\end{matrix} + KCN = \begin{matrix}CH_2CN\\|\\CO_2K\end{matrix} + KCl.$$

Potassium cyanacetate.

$$\begin{matrix}CH_2CN\\|\\CO_2K\end{matrix} + 2H_2O + 2HCl = \begin{matrix}CH_2.CO_2H\\|\\CO_2H\end{matrix} + NH_4Cl + KCl.$$

Malonic acid.

Malonic acid is a colourless, crystalline substance which melts at 132° and dissolves readily in water, alcohol, and in ether. On being heated to 140°–150°, it loses carbon dioxide and is converted into acetic acid. This is a characteristic property of all polybasic acids having two carboxyl groups attached to the same carbon atom:

$$\begin{matrix}CH_2.CO_2H\\|\\CO_2H\end{matrix} = \begin{matrix}CH_3\\|\\CO_2H\end{matrix} + CO_2.$$

Malonic acid. Acetic acid.

EXPT. 90.—Heat a little malonic acid in a test-tube until it melts and effervesces, and decant the gas given off into lime-water. The presence of carbon dioxide is shown by the turbidity of the lime-water, whilst the liquid which remains in the test-tube has the smell of acetic acid.

Succinic acid, $CO_2H.CH_2.CH_2.CO_2H$, is mentioned by Agricola (1550) as being obtained from amber (Lat. *succinum*) by distillation, and the method is still used in its preparation. When amber is distilled in iron retorts the acid collects in the receiver, partly in the solid form and partly in solution, together with an oil, known as **amber oil.** The distillate is then filtered from the oil and evaporated. Succinic acid occurs in certain lignites and fossil wood, and in lettuces, unripe grapes, and wormwood. It is also obtained by the fermentation of calcium malate, or ammonium tartrate, by yeast or putrid cheese. The

process is one of reduction, and may be imitated by the actio of strong hydriodic acid:

CH(OH).CO.OH | CH(OH).CO.OH	CH(OH).CO.OH | CH_2.CO.OH	CH_2.CO.OH | CH_2.CO.OH
Tartaric acid.	Malic acid.	Succinic acid.

When either tartaric or malic acid is heated with stron hydriodic acid, it is converted into succinic acid, just as glycolli acid under the same conditions forms acetic acid (p. 170). Suc cinic acid has also been synthesised by a method which leave no doubt as to its constitution. When ethylene dibromide i boiled with potassium cyanide, ethylene cyanide is formed. Th latter, on hydrolysis, gives succinic acid. As ethylene dibromid is prepared from ethylene, and ethylene may be obtained fron acetylene, which is formed by the direct union of carbon an hydrogen, succinic acid can be synthesised from its elements:

CH ‖	$\xrightarrow{H_2}$	CH_2 ‖	$\xrightarrow{Br_2}$	CH_2Br |	$\xrightarrow{KCN}$	CH_2CN |	$\xrightarrow{H_2O}$	CH_2.CO.OH |
CH		CH_2		CH_2Br		CH_2CN		CH_2.CO.OH
Acetylene.		Ethylene.		Ethylene bromide.		Ethylene cyanide.		Succinic acid.

Succinic acid crystallises in prisms, or plates, which melt a 182°. When distilled it is converted into the anhydride, a white crystalline substance, which melts at 120°.

$$\begin{matrix} CH_2.CO \\ | \quad >O \\ CH_2.CO \end{matrix}$$

Succinic anhydride.

HYDROXY-DIBASIC ACIDS

Malic acid, Hydroxysuccinic acid, $CO_2H.CH(OH).CH_2.CO_2H$ —The acid was isolated by Scheele, in 1785, from the juic of unripe apples (Lat. *malum*), and it frequently accom panies tartaric and citric acid (pp. 184, 191) in fruits, partly in the free state and partly as the potassium or calcium salt In currants, cherries, and in the leaves and stems of rhubarb

it is present as the acid potassium salt; in the tobacco plant, as the acid calcium salt.

Malic acid is usually prepared from the unripe berries of the mountain ash. The juice is boiled with milk of lime which precipitates the neutral calcium salt, $C_4H_4O_5Ca$. The precipitate is collected and washed, and recrystallised from hot, dilute nitric acid, from which the acid salt separates, $(C_4H_5O_5)_2Ca+6H_2O$. This is decomposed with the theoretical quantity of oxalic or sulphuric acid, and the liquid, filtered from the calcium oxalate or sulphate, is concentrated by evaporation. Malic acid is a crystalline substance which melts at about 100°. It is very hygroscopic, and deliquesces on exposure to moist air.

The structure of malic acid has been determined in various ways. The acid is readily reduced by hydriodic acid to succinic acid, and is therefore a derivative of succinic acid. When monobromosuccinic acid is acted upon with moist silver oxide, it is converted into malic acid. It is therefore hydroxysuccinic acid:

$$\begin{array}{l} OH|Ag+Br|CH.CO_2H=(OH)CH.CO.OH \\ \qquad\qquad\quad | \qquad\qquad\quad | \\ \qquad\qquad CH_2.CO_2H \qquad CH_2.CO_2H \end{array} +AgBr$$

Monobromosuccinic acid. Malic acid.

Moreover, hydrobromic acid yields monobromosuccinic acid; phosphorus chloride, monochlorosuccinic acid; and acetyl chloride, acetyl malic acid:

$$\begin{array}{l} C_2H_3O.OCH.CO.OH \\ \qquad\qquad | \\ \qquad\qquad CH_2.CO.OH. \end{array}$$

Acetyl malic acid.

All these reactions give evidence of the presence of a hydroxyl group in the acid. The natural acid from berries is lævorotatory in dilute solution, which points to the existence of an asymmetric carbon atom. The corresponding dextro-rotatory acid is obtained by the partial reduction of ordinary tartaric acid (see p. 186) with hydriodic acid. The existence of these two acids receives the same explanation as that of the two lactic acids. The space configuration of the two isomers is represented in Fig. 51.

The synthetic malic acids obtained from bromosuccinic acid and by the reduction of inactive racemic acid (p. 186) are inactive, and consist of a mixture of equal quantities of the two active components. It is usual to find the artificial products of the laboratory, prepared from inactive materials, to be themselves inactive; and this is readily understood when we consider that there is only a single property, the action on polarised light, which distinguishes the two components. Chemically they are identical, and therefore, in any chemical change, the formation of one isomer necessitates, under ordinary conditions, the production of an equal quantity of the second.

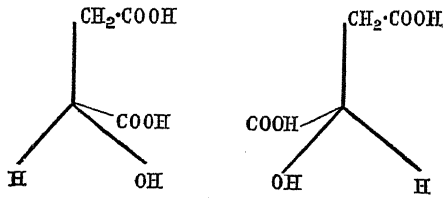


FIG. 51.—Space configuration of isomeric Malic acids.

Tartaric acid, Dihydroxysuccinic acid, $CO_2H.CH(OH).CH(OH).CO_2H$.—Tartaric acid in the form of the acid potassium salt has been known since wine was made from grapes. It is deposited during fermentation as a brown, crystalline crust, known as **argol**, or wine-lees. The term **tartar** was given by the alchemists to both animal and vegetable concretions, and wine-lees, stone, gravel, and the deposit on teeth, being attributed to the same cause, received the same name. Tartaric acid was isolated and recognised as a distinct acid in 1769 by Scheele, who described it in his first scientific paper. As the free acid and as the acid potassium salt it is widely distributed throughout the vegetable kingdom. It is found with malic acid in the berries of the mountain ash, and in other berries and fruits, but the chief source is grape juice. During fermentation the acid potassium salt in the juice is rendered insoluble by the alcohol, and gradually separates in minute crystals which carry down some of the colouring matter of the wine. The brown powder,

or argol, is recrystallised for the production of the pure salt, which is known as **cream of tartar.**

In order to prepare tartaric acid, the argol is dissolved in water, and chalk is added until the solution is nearly neutralised. The insoluble calcium tartrate which is deposited is separated by filtration from the neutral potassium tartrate which is in solution. A further quantity of calcium tartrate is obtained from the filtrate by adding calcium chloride. The process is represented by the following equations:

$$\underset{\text{Acid potassium tartrate.}}{2C_4H_5O_6K} + CaCO_3 = \underset{\text{Calcium tartrate.}}{C_4H_4O_6Ca} + \underset{\text{Potassium tartrate.}}{C_4H_4O_6K_2} + CO_2 + H_2O.$$

$$C_4H_4O_6K_2 + CaCl_2 = C_4H_4O_6Ca + 2KCl.$$

The calcium tartrate is then decomposed by the addition of sulphuric acid, and the solution, filtered from calcium sulphate, is concentrated and allowed to cool, when crystals of tartaric acid separate. The potassium chloride is recovered and used in the manufacture of potash salts.

Tartaric acid crystallises in large, transparent prisms, which dissolve in water and alcohol and melt at 205°. It is dextro-rotatory in aqueous solution. When heated with potassium hydrogen sulphate, it yields pyruvic acid (p. 176).

Salts of Tartaric acid.—Tartaric acid forms acid and neutral salts and salts with two different bases. The acid salts of potassium and ammonium are sparingly soluble in cold water.

EXPT. 91.—Add a little potassium nitrate, or acetate, solution and a few drops of dilute acetic acid to a strong solution of tartaric acid, and stir with a glass rod. The acid potassium salt of tartaric acid is precipitated. A similar precipitate is formed when ammonium salt is used in place of the potassium salt.

The neutral salts of the alkalis are all readily soluble in water. **Rochelle salt,** or potassium sodium tartrate, $C_4H_4O_6KNa + 4H_2O$, so called after its discoverer, Seignette de la Rochelle, is prepared by neutralising a solution of cream of tartar with sodium carbonate solution. The solution is then evaporated, and deposits, on cooling, large transparent crystals. **Tartar emetic,** $C_4H_4O_6K(SbO) + \frac{1}{2}H_2O$, is prepared by dissolving antimonious oxide in a solution of cream of tartar. It crystallises in rhombic octahedra. It dissolves

in water, and is used in medicine as an emetic and in cotton dyeing as a mordant (p. 58).

Detection of Tartaric acid.—Tartaric acid is detected by the formation of the insoluble calcium salt, $C_4H_4O_6Ca + 4H_2O$, on the addition of calcium chloride to the neutral solution. The calcium salt is distinguished from calcium oxalate by its solubility in caustic alkalis and acetic acid. It may also be detected by Fenton's reaction.

EXPT. 92.—**Fenton's reaction.**—Dissolve a neutral salt of tartaric acid in water. Add a drop of ferrous sulphate solution, a few drops of hydrogen peroxide solution, and make alkaline with caustic soda. A violet solution is obtained.

When tartaric acid or its salts are strongly heated they char and emit an odour of burnt sugar.

A further test is the reduction of silver tartrate in alkaline solution as follows :—

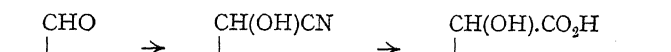
EXPT. 93.—Dissolve some Rochelle salt or other neutral salt in water, and add a solution of silver nitrate. A white precipitate of silver tartrate is thrown down. Add dilute ammonia solution drop by drop until the precipitate nearly vanishes, and place the vessel in a beaker of hot water. A mirror of silver is deposited.

Structure of Tartaric acid.—The salts described above show tartaric acid to be a dibasic acid. Moreover, tartaric acid readily forms mono- and di-alkyl esters—viscid liquids, which can be distilled without decomposition under reduced pressure. These esters combine with acid chlorides and form mono- and di-acyl esters; whilst strong nitric acid gives a dinitroxy-ester. Taken in conjunction with the fact that tartaric acid undergoes reduction to malic and succinic acids (p. 183), the formation of acyl esters affords additional evidence of the acid being a dihydroxysuccinic acid:

$CH(OH).CO_2C_2H_5$	$(C_2H_3O).OCH.CO_2C_2H_5$	$(NO_2)O.CH.CO_2C_2H_5$
$CH(OH).CO_2C_2H_5$	$(C_2H_3O).OCH.CO_2C_2H_5$	$(NO_2)O.CH.CO_2C_2H_5$
Diethyl tartrate.	Diacetyl tartaric ester.	Dinitroxy-tartaric ester.

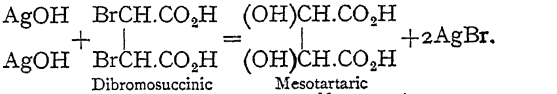
Racemic acid, $C_4H_6O_6$.—A second acid, isomeric with ordinary tartaric acid, is sometimes found in the mother liquors from cream of tartar, and can be obtained by heating tartaric

acid with water in a sealed tube to 175° or by boiling with strong caustic soda solution. It is known as **racemic acid** and melts at 205°. It has been synthesised from glyoxal by forming the dicyanhydrin and hydrolysing the product:



Some of the salts of racemic acid have a different crystalline form and contain a different amount of water of crystallisation from those of the ordinary acid, and the calcium salt is less soluble in water, but, like tartaric acid, it yields succinic acid on reduction. The main point of distinction is that racemic acid is optically inactive in solution. It is clear that we are dealing with a case of stereo-isomerism.

Mesotartaric acid, $C_4H_6O_6$.—A third acid, isomeric with tartaric and racemic acid, is formed together with racemic acid by heating ordinary tartaric acid with water to 165° or with caustic soda. It has been obtained synthetically by the action of silver hydroxide on dibromosuccinic acid.



Mesotartaric acid crystallises in rectangular tables with one molecule of water. It melts at 140° and is more soluble than racemic acid. The most characteristic salt of this acid is calcium mesotartrate, $C_4H_4O_6Ca+3H_2O$, which is insoluble in acetic acid and much less soluble in water than ordinary calcium tartrate. It is optically inactive.

Stereo-isomerism of the Tartaric acids.—The relationship of the three tartaric acids was first explained by Pasteur (1860). In examining the crystalline form of sodium ammonium tartrate, Pasteur observed that the crystals exhibited hemihedral facets—that is, facets of which only half the full number required by the symmetry of the crystal form are present. Assuming that optical activity in ordinary tartaric acid was in some way related to the presence of these facets, he crystallised the same salt of racemic acid which is inactive, anticipating that the

inactive salt would exhibit a symmetrical, crystalline structure. The crystals, however, showed the unsymmetrical facets of the ordinary acid; but the crystals were not identical, some having their facets situated on one side, some on the opposite side of the crystal. Crystals which bear the relation of object and image are known as **enantiomorphous** forms. The two kinds of crystals are drawn in Fig. 52 in which the hemihedral facets are indicated by shading.

Pasteur separated the two kinds of crystals, dissolved them in water, and examined them in the polarimeter. They were found to deviate the plane of polarisation in opposite directions, and to the same amount. The dextro-rotatory variety was identical with the salt of ordinary tartaric acid; the lævo-

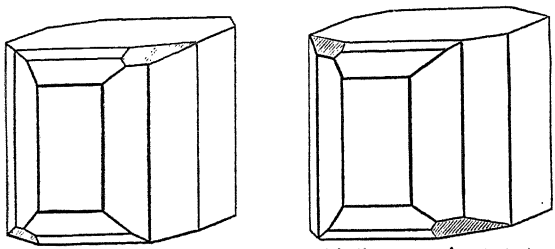
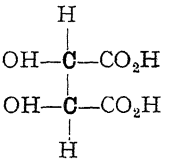


FIG. 52.—Enantiomorphous crystal forms of Sodium ammonium tartrate.

rotatory crystals represented a fourth variety. Lævo-tartaric acid is identical with the dextro-compounds in all respects except in its action on polarised light. Racemic acid, like lactic acid, therefore represents a mixture, or, more correctly, a compound, of an equal number of molecules of the dextro- and lævo-forms. That crystallised racemic acid and its salts must be regarded rather as compounds than mixtures is shown from their chemical and physical properties, which are distinct from those of either of the components. The same thing holds with regard to the salts of ordinary and sarcolactic acids (p. 174). Under certain conditions these acids and salts may be resolved into their active components (p. 190). An inactive substance which shows physical characters distinct from its constituent active components is known as a **racemic** compound.

We have still to account for the isomerism of mesotartaric

acid. If we examine the structural formula of tartaric acid, it will be seen that it possesses two asymmetrical carbon atoms. These are denoted in the formula by thick type.



Each asymmetrical carbon atom is surrounded by the same groups. Let us suppose that each asymmetrical carbon with its associated groups produces a certain rotation in a given direction, we may imagine the following combinations of two similar asymmetric groups. Both produce dextro-rotation or both produce lævo-rotation. These will represent the dextro- and lævo-varieties, and the mixture of the two will produce inactive racemic acid. Racemic acid is said to be inactive by **external compensation.** Suppose, finally, the two asymmetric

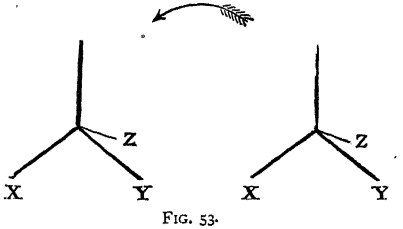
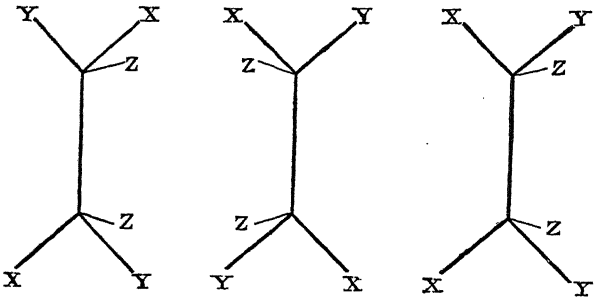


FIG. 53.

groups produce rotation in opposite directions. They will neutralise one another. The result will be a compound which is inactive by **internal compensation.** Such a compound cannot be resolved by any process into its active components. This represents mesotartaric acid, which is permanently inactive, never having been resolved. The explanation is more easily followed by means of models. Suppose that Fig. 53 represents the two asymmetric carbon atoms, and that the bonds lettered X, Y, Z, stand for the three groups H, OH, and CO.OH, for which coloured sticks may be employed. Join together two identical models

by bringing one on to the top of the other (Fig. 53). If we suppose each model to be dextro-rotatory, the combination will also be dextro-rotatory, and may stand for the dextro-acid, I., Fig. 54.

The mirror image of this is shown at II, Fig. 54, and will stand for the lævo-acid. It is impossible, of course, to establish any direct connection between the character of the rotation and the particular grouping. All we can do is to make an arbitrary choice, and let I stand for the dextro-, then II represents the lævo-acid. The mixture represents racemic acid. In meso-



I. Dextro-tartaric acid. II. Lævo-tartaric acid. Racemic acid. III. Meso-tartaric acid.

FIG. 54.

tartaric acid (III) the top and bottom asymmetric groups stand in the relation of object and mirror image, and consequently their rotations are opposed and neutralised.

Stereo-isomerism in relation to the number of asymmetric carbon atoms.—From the foregoing it will be seen that every additional asymmetric carbon atom produces a rapidly increasing number of possible stereo-isomers, which may be easily determined by a simple calculation. Glucose contains 4 asymmetric carbon atoms. The theoretical number is 16 stereo-isomers, of which 14 are known, mannose and galactose being among this number.

The resolution of externally-compensated compounds.—The principal methods for resolving inactive substances into their active components are due to Pasteur. The separation by

the aid of the enantiomorphous crystalline forms of the salts has already been explained in the case of racemic acid; but the method is limited in its application by the fact that well-defined crystals which exhibit hemihedral facets cannot always be obtained. A more serviceable method is to combine the inactive substance, which is to be resolved, with an optically active compound; if a base, with an active acid; or, if an acid, with an active base. The solubilities of the salts of dextro- and lævo-tartaric acid with the same active base, such as strychnine or brucine (p. 321) are not the same, and can be separated by fractional crystallisation. For resolving racemic acid, the racemate of an active base is prepared, and the salt crystallised. The less soluble portion, which first crystallises, is the salt of one acid, and the more soluble that of the other. This process has been applied successfully to the resolution of inactive lactic acid, and to many other cases. A third method, also employed by Pasteur, is to cause a solution of the inactive substance to ferment, by introducing certain low vegetable organisms, such as yeast, moulds, or bacteria; one of the two active forms is, as a rule, more easily assimilated than the other, and the liquid shows increasing optical activity as the fermentation proceeds. Artificial fructose, like most laboratory products obtained from inactive materials, is inactive; but, when fermented with yeast, the natural fructose is assimilated whilst the dextro-rotatory sugar remains. In this way a dextro-rotatory fructose has been prepared.

Citric acid, $C_6H_8O_7+H_2O$, is present as the free acid in lemon juice, and in the juice of oranges, limes, sloes, etc. It is found with malic acid in gooseberries, currants, and other fruits, and with malic and tartaric acids in mountain-ash berries. It also occurs as the calcium and potassium salts in many plants. It is obtained from lemon juice, which contains 7–8 per cent. of the acid, by neutralising with chalk or lime, and boiling the liquid. The calcium salt, which is insoluble in hot water, is thrown down and filtered. It is then decomposed with sulphuric acid. On evaporating the filtrate from calcium sulphate, citric acid crystallises in large, transparent crystals containing 1 molecule of water. Lemon juice, which contains the acid, should

not be confounded with oil of lemons, which is obtained from the rind, and contains substances belonging to the family of terpenes (p. 260).

Citric acid is now prepared on an industrial scale by the citric fermentation of glucose, whereby 50 per cent. of the glucose is converted into citric acid. The ferment is a fungus which breaks up the glucose into citric acid and carbon dioxide. Citric acid is a tribasic acid, and forms three series of salts. The potassium and sodium salts of citric acid can be prepared containing 1, 2, and 3 atoms of the metal in place of hydrogen. The calcium salt, $(C_6H_5O_7)_2Ca_3 + 4H_2O$, is characteristic of the acid. It is not precipitated on adding lime-water to a cold solution of citric acid, or calcium chloride to a citrate; but on boiling, the calcium salt, which is less soluble in hot water than cold, is thrown down. In this way the acid may be distinguished from some of the other acids derived from vegetable sources.

Ferric ammonium citrate is prepared for medicinal purposes in thin, transparent flakes, by evaporating a solution of ferric citrate in ammonia on glass plates, and breaking up the hard film which remains.

The structure of citric acid, as determined by its decomposition products and synthesis, is represented by the formula:

$$\begin{array}{l} CH_2.CO_2H \\ | \\ CH(OH).CO_2H\,. \\ | \\ CH_2.CO_2H \end{array}$$

Formula of citric acid.

UNSATURATED MONOBASIC ACIDS

Acrylic acid, $CH_2{:}CH.CO.OH$, is the simplest member of the important group of unsaturated fatty acids. It is formed in a variety of ways; by the oxidation of acrolein (p. 143); by the action of alcoholic potash on α- or β-bromopropionic acid and by heating hydracrylic acid, or hydroxypropionic acid, $CH_2(OH).CH_2.CO_2H$ (p. 175):

$$\underset{\text{α-Bromopropionic acid.}}{CH_3.CHBr.CO_2H} + KOH = \underset{\text{Acrylic acid.}}{CH_2{:}CH.CO_2H} + KBr + H_2O.$$

$$\underset{\text{Hydracrylic acid.}}{CH_2OH.CH_2.CO_2H} = \underset{\text{Acrylic acid.}}{CH_2{:}CH.CO_2H} + H_2O.$$

Acrylic acid is a liquid with a pungent smell, which boils at 140°. It possesses the properties of an unsaturated compound. On reduction, it yields propionic acid; with bromine it forms dibromopropionic acid; with hydrochloric acid it gives β-chloropropionic acid. In the latter case it should be noted that the halogen attaches itself to the carbon farthest from the carboxyl, which is the general rule when halogen acids unite with unsaturated acids.

$CH_2Br.CHBr.CO.OH.$ — Dibromopropionic acid.

$CH_2Cl.CH_2.CO_2H.$ — β-Chloropropionic acid.

Oleic acid, $C_{18}H_{34}O_2$, has already been referred to under fats and oils (p. 118); but belongs strictly to the acrylic acid series. In animal fat, olive oil and other vegetable oils, it is present as the glyceride or olein. Its lead salt is soluble in ether, and this property is utilised for separating it from stearic and palmitic acid, the lead salts of which are insoluble. Its relationship to stearic and palmitic acids as well as its unsaturated character are clearly exhibited by the following reactions. It is reduced by nickel in presence of hydrogen to stearic acid (fat hardening process), and oxidised by fusion with caustic potash to palmitic acid and acetic acid:

$$\underset{\text{Oleic acid.}}{C_{18}H_{34}O_2} + H_2 = \underset{\text{Stearic acid.}}{C_{18}H_{36}O_2}.$$

$$C_{18}H_{34}O_2 + 2KOH = \underset{\substack{\text{Potassium}\\\text{palmitate.}}}{C_{16}H_{31}O_2K} + C_2H_3O_2K + H_2.$$

It forms additive compounds with iodine, bromine, and also with strong sulphuric acid.

EXPT. 94.— Add a few drops of a solution of bromine in carbon tetrachloride to oleic acid or olein and shake up. The colour is at once discharged.

When the compound with sulphuric acid is distilled with steam, it is converted into a solid isomer of oleic acid, known as **isoleic acid,** which can be used like stearic and palmitic acid in candle-making. This constitutes one of the advantages of the sulphuric acid saponification process, as by this means a larger output of solid acids is obtained than by the other saponification methods. Another solid isomer, **elaidic acid,** is obtained by treating oleic acid with nitrous acid.

EXPT. 95.—Pour a few c.c. of oleic acid into a test-tube and a a small piece of sodium nitrite and a drop or two of strong nit acid. Nitrous acid is evolved, and in a few minutes the oleic ac is converted into solid elaidic acid. A similar change occurs wi olive oil.

The formation of these isomers may be explained either a change produced in the position of the double bond in t chain of carbon atoms or by some difference in the space arrang ment of the atoms.

Linoleic acid, $C_{18}H_{32}O_2$, is present as the glyceride, togeth with the glycerides of linolenic acid, $C_{18}H_{30}O_2$, and other u saturated acids, in the so-called **drying oils**, *e.g.* linseed (from fla cotton-seed, and colza (rape-seed) oils. These oils possess t property of absorbing oxygen from the air and changing in transparent, resinous substances. The change is hastened b heating the oil with certain metallic compounds known as **drier** such as lead oxide, manganese borate, etc. When linseed o is thus treated it is known as **boiled linseed oil.**

Linseed oil.—The boiled oil is used as a vehicle for pigment and forms, when dry, a hard, protective, and at the same tin transparent, covering. By pouring successive layers of the o on to cloth or canvas and freely exposing them to the air, the o hardens and forms the material known as **oil-cloth. Linoleu** is produced in a similar manner by first oxidising the heated o by blowing a current of air or oxygen through the liquid, there forcing it into a fine spray. The semi-solid, gelatinous product melted and mixed with powdered cork and other materials, a spread out in thin layers, which on cooling become solid.

The absorption of oxygen by drying oils is generally accor panied by a considerable rise of temperature, and fires ha been known to originate through the spontaneous ignition cotton waste which has become impregnated with oil in t cleaning of machinery.

Varnishes are also made from boiled linseed oil, by mixing with certain gums or resins and diluting with turpentine or spir of wine.

QUESTIONS ON CHAPTER XV.

1. Describe the methods of preparing the hydroxy-acids of the fatty series. Give some account of their properties.

2. What is the action of hydrogen cyanide on ketones and aldehydes? Mention two examples in which this action has been utilised in effecting the synthesis of important organic compounds.

3. Show how lactic acid may be produced from propionic acid and from aldehyde, and how these substances may be obtained from lactic acid.

4. Describe the properties of the hydroxy-acids. What is the action of phosphorus chloride, hydrobromic acid, hydriodic acid, and nitric acid on glycollic acid?

5. Several acids are known having the composition expressed by the formula $C_3H_6O_3$. Expand this into the several constitutional formulæ. What facts go to prove that lactic acid is both acid and alcohol?

6. Describe how ethylene- and ethylidene-lactic acids may be obtained synthetically. What is the result of heating each variety? Which exhibits optical isomerism? Give a brief account of the theory which is generally accepted as accounting for this kind of isomerism.

7. Give an example of an aldehydic and a ketonic acid, and describe some of their characteristic properties.

8. What is the action of sodium on ethyl acetate? Indicate how the resulting product may be made the means of obtaining (*a*) a substituted acetic acid, (*b*) a substituted acetone.

9. What do you understand by the term optical activity? Explain its connection with the constitution of carbon compounds which manifest this property.

10. By what means are acids of the succinic series prepared from acids of the acetic series?

11. Describe any method by which an acid of the succinic series may be converted into a higher homologue of the same series.

12. How would you proceed to make oxalic acid from (*a*) common sugar, (*b*) oxamide, (*c*) formic acid?

13. How is oxalic acid made on the large scale? What reactions occur between oxalic acid and (*a*) alcohol, (*b*) sulphuric acid, (*c*) phosphorus pentachloride?

14. What is the formula of oxalic acid? How is it made? How can ammonium oxalate be prepared? What is its relationship to cyanogen?

15. Starting from acetic acid, how would you prepare the diethyl

ester of malonic acid, and how would you obtain acetic acid fro the ester ?

16. An acid which contains only carbon, hydrogen, and oxyg gave on analysis 40·7 per cent. of carbon and 5·08 per cent. hydrogen. The silver salt contained 65 per cent. of silver. T acid on heating evolved carbon dioxide, leaving a strongly ac liquid. What is the probable composition of the acid and of t product formed on heating, and how is the former most easi prepared ?

17. What are the chief natural sources and chemical relatio ships of succinic, malic, and tartaric acids ? How may these aci be changed into each other ?

18. How many tartaric acids are known ? How are the obtained ? How do you account for their existence ?

19. Starting from ethylene, show by what series of operatio tartaric acid may be built up. In what respect does the acid s formed differ from tartaric acid obtained from grapes ?

20. Tartaric acid contains six atoms of oxygen, but is onl dibasic. In what forms does the oxygen exist in this acid, an how is such a question determined ?

21. What is the common source and mode of manufacture c citric acid ?

22. What is meant by the term unsaturated acid ? Giv examples. How would you show that an acid is unsaturated ?

23. What is meant by the term *drying oils*, and what are the applications ?

CHAPTER XVI

SOME NITROGEN COMPOUNDS

Acetamide.—On page 63 it was stated that by the action of ammonia on acetyl chloride acetamide is formed.

A convenient method for preparing acetamide is to distil ammonium acetate:

$$CH_3.CO_2NH_4 = CH_3.CONH_2 + H_2O.$$

The operation is conducted as follows:

EXPT. 96.—**Preparation of Acetamide.**—Melt 50 grams of ammonium acetate by gently heating, and pour the liquid into a round flask. Add 60 c.c. glacial acetic acid and boil gently with

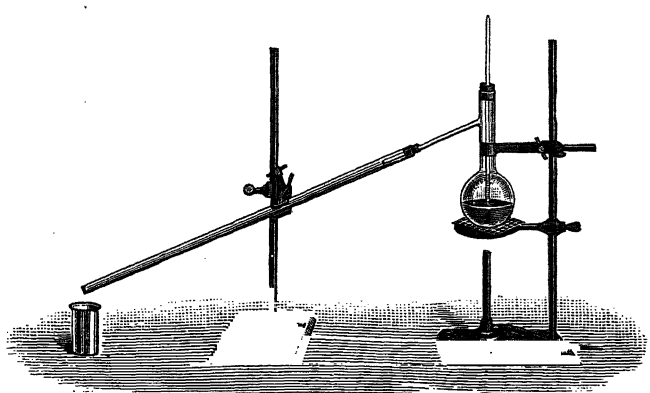


FIG. 55.—Preparation of Acetamide.

a reflux condenser for four hours. The product is distilled as follows:—Insert a thermometer into the neck of a distilling flask, and use a long wide tube as a condenser (Fig. 55). Heat over wire-

gauze. A certain quantity of ammonia, water, and acetic acid distils. When the temperature reaches 213°, change the receiver the distillate on cooling solidifies and consists mainly of acetamide Acetamide melts at 82° and boils at 222°. The smell, like that o mice, proceeds from a minute trace of impurity.

The presence of nitrogen in the acetamide may be detected a follows:

EXPT. 97.—**Tests for Nitrogen in organic compounds.**—(1) Pou about 10 c.c. of distilled water into a small beaker. Place abou half a gram of acetamide in a small test-tube along with a piec of metallic sodium the size of a coffee bean, and heat them, a first gently, until the reaction subsides, and then strongly, until the glass is nearly red-hot. Place the hot end of the tube in the smal beaker of water. The glass crumbles away, and any residua sodium is decomposed with a bright flash; the cyanide which is formed rapidly goes into solution, whilst a small quantity of carbon remains suspended in the liquid. Filter through a small filter into a test-tube. Pour into the clear solution about 1 c.c. of ferrous sulphate solution (to which a drop of ferric chloride has been added) boil for a minute, cool, and acidify with dilute hydrochloric acid. A precipitate of Prussian blue indicates the presence of nitrogen. (2) Another test is to heat the substance with soda-lime when ammonia is evolved. Grind up a small quantity of acetamide with 2-3 times its bulk of soda-lime and bring the mixture into a test-tube. Place a little soda-lime above the mixture and then heat strongly. Ammonia will be evolved.

Reactions of Acetamide.—The amides are characterised by certain distinctive properties. On boiling with caustic soda they are hydrolysed. Acetamide is converted into acetic acid and ammonia:

$$CH_3.CO.NH_2 + NaOH = CH_3.CO_2Na + NH_3.$$

EXPT. 98.—Boil a small quantity of acetamide with caustic soda solution in a test-tube, and smell the vapour given off, or test it with red litmus. Ammonia is evolved, and sodium acetate is found in solution—

By the action of dehydrating agents (*e.g.* phosphorus pentoxide) the amides are converted into alkyl cyanides. Acetamide, when mixed with phosphorus pentoxide and distilled, gives methyl cyanide:

$$\underset{\text{Acetamide.}}{CH_3.CO.NH_2} - H_2O = \underset{\text{Methyl cyanide.}}{CH_3CN}.$$

EXPT. 99.—**Preparation of Methyl cyanide or Acetonitrile.**—Mix together 10 grams of dry acetamide and 15 grams of phosphorus pentoxide in a small retort or distilling flask attached to a condenser and receiver. Heat the mixture over a small flame. Collect the liquid which distils, and add a few c.c. of water and then solid potassium carbonate, until no more dissolves. The upper layer of liquid is removed and redistilled over fresh phosphorus pentoxide. Methyl cyanide boils at 82°.

As we have already seen, the cyanides—hydrocyanic acid and methyl cyanide—give acids on hydrolysis (p. 78):

$$CH_3.CN + 2H_2O = CH_3.CO_2H + 2NH_3.$$

Thus, the conversion of ammonium acetate into methyl cyanide forms a cycle of reversible changes:

$$\underset{\text{Ammonium acetate.}}{CH_3.CO.ONH_4} \rightleftharpoons \underset{\text{Acetamide.}}{CH_3.CO.NH_2}$$

$$\nwarrow\searrow \quad \nearrow\swarrow$$

$$\underset{\text{Methyl cyanide.}}{CH_3.CN}$$

A third reaction of the amides is their behaviour with bromine and caustic soda.

It takes place in two steps. By the action of bromine, acetamide is converted into acetobromamide:

$$CH_3.CONH_2 + Br_2 = \underset{\text{Acetobromamide.}}{CH_3.CONHBr} + HBr.$$

If the acetobromamide is then warmed with excess of potash, it is converted into methyl isocyanate, which further breaks up, on boiling, into methylamine. In the first reaction the hydrobromic acid is removed from the acetobromamide, which produces methyl isocyanate by atomic rearrangement. The methyl isocyanate is then hydrolysed (Hofmann):

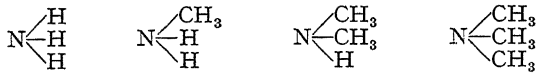
$$\underset{\text{Acetobromamide.}}{CH_3.CONHBr} + KOH = \underset{\text{Methyl isocyanate.}}{CH_3N:CO} + KBr + H_2O.$$

$$CH_3.N:CO + 2KOH = \underset{\text{Methylamine.}}{CH_3NH_2} + K_2CO_3.$$

EXPT. 100.—Mix together in a $\frac{1}{4}$ litre flask 2 grams of acetamide and 2 grams of bromine, and then cool and add dilute caustic potash solution until the colour of the bromine vanishes. Now

add 6 c.c. of a strong potash solution and warm. There is a brisk effervescence and evolution of methylamine, which has a strong smell of herring brine (p. 205).

The Amines.—The name **amine** is given to derivatives of ammonia in which one or more atoms of hydrogen are replaced by alkyl groups. They are also called **substituted**, or **compound**, ammonias, and from their resemblance to ammonia and the caustic alkalis generally, constitute one of the groups of **organic bases.** If one, two, and three atoms of hydrogen in ammonia are replaced by alkyl groups, the compounds are known as mono-, di-, and tri-alkylamines, and also by the names, **primary, secondary,** and **tertiary** amines. The methyl derivatives of ammonia have the following structural formulæ and names:



Methylamine (Primary amine). Dimethylamine (Secondary amine). Trimethylamine (Tertiary amine).

Although the existence of substituted ammonias was foretold by Liebig as early as 1842, it was not until 1849 that Wurtz prepared the first member, methylamine, by boiling the methyl ester of cyanic acid, or methyl isocyanate (p. 199), with caustic potash. He found that the gas evolved had a strong ammoniacal smell, but differed from ammonia in being inflammable:

$$\underset{\text{Methyl isocyanate.}}{CH_3N{:}CO} + OH_2 = \underset{\text{Methylamine.}}{CH_3NH_2} + CO_2.$$

The carbon dioxide forms potassium carbonate with the potash present, and the methylamine is liberated as a gas.

EXPT. 101.—Mix together in a hard glass test-tube one part of methylamine hydrochloride and two parts of quicklime or soda-lime and heat. The methylamine gas which is evolved may be ignited, and burns with a lambent, bluish flame.

Properties of the Amines.—The amines have properties like those of ammonia. The hydrochloride, nitrate, and sulphate of methylamine have a similar composition to the salts of ammonia:

$NH_2.CH_3.HCl$	$NH_2.CH_3.HNO_3$	$(NH_2.CH_3)_2.H_2SO_4$.
Methylamine hydrochloride.	Methylamine nitrate.	Methylamine sulphate.

The amines also form double salts with the chlorides of platinum, gold, and mercury. The platinum salts of the amines are yellow, crystalline substances, closely resembling in appearance ammonium chloroplatinate, and they are similarly constituted. Methylamine chloroplatinate has the formula:

$$(NH_2CH_3.HCl)_2PtCl_4.$$

The platinum salts are readily prepared by dissolving the amine in moderately strong hydrochloric acid and adding platinic chloride. These salts can serve for determining the molecular weight of the amine by igniting a weighed quantity and estimating the residual platinum. Knowing these two weights and the atomic weight of platinum, the molecular weight of the salt is given from which that of the base can be estimated.

EXPT. 102.—If methylamine hydrochloride is not available, aniline, $C_6H_5NH_2$ (p. 262), may be used. Dissolve 0·5 c.c. in about 2 c.c. of conc. hydrochloric acid and 2 c.c. of water and add a few drops of platinic chloride. A yellow, crystalline salt, $(C_6H_5NH_2HCl)_2PtCl_4$, will gradually separate. For the determination of molecular weights by this method see p. 322.

The lower members of the series of amines, such as methylamine, dimethylamine, and trimethylamine, are gases, which dissolve in water; the higher members are either colourless liquids or solids, the solubility of which rapidly decreases with increasing molecular weight. The more volatile amines have a strong ammoniacal smell.

As the hydrochlorides and nitrates of the amines are very soluble in water, amines (which are themselves insoluble) dissolve readily on the addition of dilute hydrochloric or nitric acid.

The following table contains a list of the first four members of the series, from which it will be observed that the boiling-points rise from the primary to the tertiary amines:

Amine.	Primary. Boiling-point.	Secondary. Boiling-point.	Tertiary. Boiling-point.
Methylamine	−6°	7°	35°
Ethylamine	19°	56°	90°
Propylamine	49°	98°	156°
Butylamine	76°	160°	215°

Primary, secondary, and tertiary Amines.—It has already been stated that the amines are divided into three classes, which are termed primary, secondary, and tertiary amines, according to whether one, two, or three hydrogen atoms in ammonia are replaced by radicals.

Each of these classes possesses certain distinctive properties by which it may be identified. The methods of identification depend upon the presence of certain groups—in reality, upon the number of hydrogen atoms of ammonia unsubstituted by radicals.

These groups may be termed primary or **amino** groups, secondary or **imino** groups, and tertiary groups:

$-NH_2$	$=NH$	$\equiv N$
Primary, or amino group.	Secondary, or imino group.	Tertiary group.

Nitrous acid is one reagent employed for distinguishing the three groups.

The primary amines combine with nitrous acid and form soluble nitrites, which resemble ammonium nitrite in being rapidly decomposed in aqueous solution on heating. But, whereas ammonium nitrite yields water and nitrogen, the primary amine forms an alcohol, water, and nitrogen.

Methylamine nitrite decomposes in aqueous solution into methyl alcohol, water, and nitrogen:

$$\begin{matrix} H|N|H_2 \\ HO|N|O \end{matrix} = H_2O + N_2 + H_2O$$

Ammonium nitrite.

$$\begin{matrix} CH_3|N|H_2 \\ HO|N|O \end{matrix} = CH_3.OH + N_2 + H_2O.$$

Methylamine nitrite.

This reaction is most conveniently carried out by dissolving the amine, or its salt, in dilute hydrochloric acid, and then adding a solution of sodium nitrite. Effervescence at once begins on warming, and nitrogen is evolved. Alcohol is then found in

solution. If the same reaction is applied to a secondary amine, no effervescence occurs on addition of sodium nitrite, but a yellow oil separates, which is called a **nitrosamine**, and is volatile in steam (p. 263). Dimethylamine forms dimethyl nitrosamine. It is formed by the following reaction:

$$(CH_3)_2NH + HONO = (CH_3)_2N.NO + H_2O.$$
Dimethyl nitrosamine.

EXPT. 103.—For this experiment methylaniline, $C_6H_5NHCH_3$, may be used. Dissolve the base in dilute hydrochloric acid by shaking, and add to the clear solution a few drops of sodium nitrite. An emulsion consisting of oily drops of the nitrosamine,

$$C_6H_5N(NO)CH_3,$$

is formed, which on shaking with ether dissolves and gives a yellow solution.

Nitrous acid is without action on the tertiary amines. The action of nitrous acid may therefore be employed for the separation of tertiary amines from secondary or primary compounds.

Primary amines may also be identified by means of the isocyanide, or carbamine reaction described on p. 103. In the reaction referred to, chloroform is detected by the smell of phenylisocyanide evolved on heating chloroform with aniline and alcoholic potash. Any primary amine may be substituted for aniline, with the formation of the corresponding alkyl isocyanide. Methylamine forms, with chloroform and potash, methyl isocyanide; ethylamine gives ethyl isocyanide, and they all possess the same disagreeable smell:

$$CH_3NH_2 + CHCl_3 + 3KOH = CH_3.NC + 3KCl + 3H_2O.$$
Methyl isocyanide.

Secondary and tertiary amines do not form isocyanides.

Quaternary Ammonium compounds.—Although tertiary amines are unchanged by many of the reagents which react with the primary and secondary amines, they possess the distinctive property of uniting with a molecule of an alkyl iodide to form what are known as **quaternary ammonium iodides.** The quaternary compounds are solid substances, which are comparatively stable, and are undecomposed by boiling caustic

alkalis. Trimethylamine and methyl iodide form tetramethy ammonium iodide:

$$N(CH_3)_3 + CH_3I = N(CH_3)_4I.$$
Tetramethyl ammonium iodide.

EXPT. 104.—To show this reaction dimethylaniline, $C_6H_5N(CH_3)_2$, may be used. On warming a mixture of equal volumes of the base and methyl iodide, the solid phenyl trimethyl ammonium iodide, $C_6H_5N(CH_3)_3I$, separates.

By the action of moist silver oxide, which reacts like silver hydroxide, on the quaternary ammonium iodide, the iodine atom is exchanged for hydroxyl, and the resulting compound is known as a **quaternary ammonium hydroxide**:

$$N(CH_3)_4I + AgOH = N(CH_3)_4.OH + AgI.$$
Tetramethyl ammonium hydroxide.

Tetraethyl ammonium iodide gives the corresponding hydroxide. These substances are soluble in water, to which they impart a strongly alkaline reaction. They behave, in fact, like ammonia. The solutions precipitate metallic oxides from solutions of metallic salts and absorb carbon dioxide from the air.

Preparation of the Amines.—There are various methods for preparing amines in addition to that already described. In the same year in which Wurtz discovered the first of the substituted ammonias, Hofmann introduced an important process for preparing the mono-, di-, and tri-alkylamines. It consisted in heating the alkyl halide with alcoholic ammonia (alcohol saturated with ammonia) in sealed tubes under pressure. The three classes of amines, as well as the quaternary compounds, are produced together. In the case of methyl iodide, the following series of reactions occurs:

$$NH_3 + CH_3I = CH_3.NH_2.HI.$$
Methylamine hydriodide.

$$CH_3.NH_2 + CH_3I = (CH_3)_2NH.HI.$$
Dimethylamine hydriodide.

$$(CH_3)_2NH + CH_3I = (CH_3)_3N.HI.$$
Trimethylamine hydriodide.

$$(CH_3)_3N + CH_3I = (CH_3)_4N.I.$$
Tetramethyl ammonium iodide.

Another method is to reduce the cyanide with sodium in alcoholic solution :

$$\underset{\text{Methyl cyanide.}}{CH_3CN} + 2H_2 = \underset{\text{Ethylamine.}}{CH_3CH_2NH_2}.$$

Methylamine, CH_3NH_2, **dimethylamine,** $(CH_3)_2NH$, and **trimethylamine,** $(CH_3)_3N$, are gases. They are all present, but chiefly dimethylamine, in the brine in which herrings have been salted, and arise from the putrefaction of the fish.

Dimethylamine and trimethylamine are also present in considerable quantity, together with other amines and methyl alcohol, among the products of the destructive distillation of molasses residues from the beet-root industry (p. 157). The amines are separated by adding hydrochloric acid, distilling off the alcohol, and evaporating the residue to dryness. When di- or tri-methylamine hydrochloride is heated in a current of hydrochloric acid gas, it yields methyl chloride and ammonium chloride :

$$NH(CH_3)_2.HCl + 2HCl = 2CH_3Cl + NH_4Cl.$$
$$N(CH_3)_3.HCl + 3HCl = 3CH_3Cl + NH_4Cl.$$

The methyl chloride obtained in this way from the beet-root residues is liquefied by compression into steel cylinders, and is used like ethyl chloride in surgery as a local anæsthetic. Its rapid evaporating causes intense cold. Under the receiver of an air-pump the temperature may be reduced to $-55°$. The presence of the methylamine bases in herring brine and molasses residues has its origin in the character of the nitrogenous constituents of animal and vegetable matter, many of which contain these basic groups, which become detached by decomposition.

The various reactions described above render it possible to pass up and down the series from one member to the next.

For example, methyl alcohol may be converted into the iodide, the cyanide, and, finally, by reduction, into ethylamine and ethyl alcohol :

$$\underset{\substack{\text{Methyl}\\\text{alcohol.}}}{CH_3OH} \xrightarrow{HI} \underset{\substack{\text{Methyl}\\\text{iodide.}}}{CH_3I} \xrightarrow{KCN} \underset{\substack{\text{Methyl}\\\text{cyanide.}}}{CH_3CN} \xrightarrow{2H} \underset{\text{Ethylamine.}}{CH_3.CH_2.NH_2} \xrightarrow{HNO_2} \underset{\substack{\text{Ethyl}\\\text{alcohol.}}}{C_2H_5.OH}$$

In order to pass from a higher to a lower member of a series, the second method may be introduced. Ethyl alcohol may be converted into acetic acid, then into acetamide (p. 197), methylamine, and methyl alcohol:

$$\underset{\text{Ethyl alcohol.}}{C_2H_5OH} \xrightarrow{O} \underset{\text{Acetic acid.}}{C_2H_4O_2} \xrightarrow{NH_3} \underset{\text{Acetamide.}}{C_2H_3O.NH_2} \xrightarrow{Br_2+KOH} \underset{\text{Methylamine.}}{CH_3.NH_2} \xrightarrow{HNO_2} \underset{\text{Methyl alcohol.}}{CH_3OH}.$$

QUESTIONS ON CHAPTER XVI.

1. Give two methods for preparing primary amines free from secondary and tertiary amines.

2. Give a method for distinguishing primary, secondary, and tertiary amines.

3. In what respects do the amines resemble ammonia ?

4. Write the formula for the hydrochloride, nitrate, sulphate, and platinochloride of triethylamine.

5. Give the structural formula of isomeric amines having the molecular formula $C_4H_{11}N$.

6. What is the action of acetyl chloride on mono-, di-, and triethylamine ?

7. How can (1) acetic acid be converted into formic acid, and (2) methyl alcohol into ethyl alcohol ?

8. Describe the technical process for preparing di- and tri-methylamine. For what purpose are they employed ?

9. Describe the properties of methylamine, and show how it may be prepared from methyl alcohol and acetamide.

10. Describe and explain the method by which you would prepare methylamine from acetamide. How would you convert methylamine into trimethylamine ?

11. Describe the reactions by which primary, secondary, and tertiary ethylamines have been obtained. How would you distinguish ethylamine, diethylamine, and triethylamine from each other ?

12. Describe the chloroform test for a primary amine, and indicate the nature of the reaction on which it depends.

13. Describe the tests for nitrogen.

CHAPTER XVII

SOME CYANOGEN COMPOUNDS

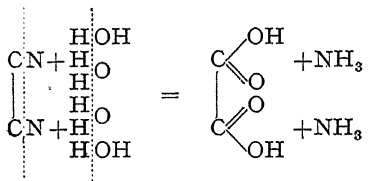
Cyanogen compounds.—Early in the eighteenth century Diesbach, a German colour maker, accidentally discovered Prussian blue by adding a salt of iron to *lixivium sanguinis* (the aqueous extract of blood calcined with potash). In 1782, Scheele obtained **prussic, or hydrocyanic, acid** from the lixivium as well as from Prussian blue by distilling them with a mineral acid; but it was not until 1815 that Gay-Lussac explained the composition of hydrocyanic acid and the cyanogen compounds. He showed that these compounds contain the group (CN) to which he gave the name **cyanogen** (κύανος, blue; γενναώ, to produce), and pointed out that cyanogen plays the part of an element like chlorine. It was, in fact, the first example of a radical (p. 38). We shall see in the course of the chapter the many points of similarity existing between cyanogen and chlorine.

Cyanogen, $(CN)_2$.—Free cyanogen was obtained by Gay-Lussac by heating mercury or silver cyanide:

$$\underset{\text{Mercuric cyanide.}}{Hg(CN)_2} = Hg + \underset{\text{Cyanogen.}}{(CN)_2}.$$

EXPT. 105.—The mercuric cyanide for the experiment is prepared by dissolving mercuric oxide in aqueous hydrocyanide acid and concentrating the solution until it crystallises. Heat a few grams of mercuric cyanide in a hard glass test-tube. A gas is evolved, which may be ignited at the mouth of the tube, and burns with a purple flame. A small quantity of a brown, amorphous powder is left, which is known as **paracyanogen,** and is a polymeride of cyanogen. As cyanogen is soluble in water, it must be collected over mercury, should this be necessary.

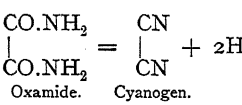
Cyanogen is a colourless gas with a peculiar smell and is very poisonous. It burns with a purple flame, forming carbon dioxide and nitrogen. Its density corresponds with the formula $(CN)_2$. Like chlorine, therefore, which in the free state consists of molecules composed of two atoms, the molecule of cyanogen is composed of two cyanogen groups, and the gas is sometimes called **dicyanogen.** Cyanogen may be readily condensed, under a pressure of four atmospheres, to a liquid. Liquid cyanogen boils at $-20°$ and solidifies at $-34°$. Cyanogen dissolves readily in water; but the solution gradually decomposes, forming a brown, flocculent precipitate, known as **azulmic acid,** whilst ammonium oxalate is found in solution. The ammonium oxalate arises from the hydrolysis of the cyanogen, a reaction which resembles that which takes place when the alkyl cyanides are hydrolysed (p. 78):



Cyanogen. Water. Oxalic acid. Ammonia.

Ammonium oxalate.

Just as methyl cyanide is obtained by dehydrating acetamide (p. 198), so, if oxamide (p. 180) is distilled with phosphorus pentoxide, cyanogen is formed:



Oxamide. Cyanogen.

EXPT. 105*a*.—Bring into a hard glass test-tube some phosphorus pentoxide to a depth of about $\frac{3}{4}$ inch and immediately add about half its bulk of oxamide. Mix thoroughly by shaking and stirring with a glass rod, and then heat. The cyanogen can be ignited at the mouth of the tube.

If cyanogen is passed into caustic potash solution, it is decomposed into potassium cyanide, potassium cyanate, and water.

This reaction brings out clearly the similarity in the properties of cyanogen and the halogens:

$$(CN)_2 + 2KOH = \underset{\text{Potassium cyanide.}}{KCN} + \underset{\text{Potassium cyanate.}}{KCNO} + H_2O.$$

$$Cl_2 + 2KOH = KCl + KClO + H_2O.$$

Hydrocyanic acid, Prussic acid, occurs in certain plants; it is found in the leaves of the cherry laurel, in bitter almonds, and in the kernels of cherry, peach, plum, and other stone fruits. It is not usually present as the free acid in the plants named, but in combination with glucose (grape-sugar) and benzaldehyde (oil of bitter almonds, p. 290) in the form of a crystalline substance known as **amygdalin.** This crystalline compound is termed a **glucoside,** and is readily decomposed by dilute sulphuric acid into its constituents. The process is one of hydrolysis:

$$\underset{\text{Amygdalin.}}{C_{20}H_{27}NO_{11}} + 2H_2O = \underset{\text{Benzaldehyde.}}{C_7H_6O} + \underset{\text{Hydrocyanic acid.}}{HCN} + \underset{\text{Glucose.}}{2C_6H_{12}O_6}.$$

The same decomposition is produced by the action of an enzyme (p. 21) known as **emulsin,** which is present in bitter almonds. Emulsin acts only in the presence of water, so that by grinding up bitter almonds with a little water, hydrolysis takes place, and the smell of hydrocyanic acid, together with that of benzaldehyde, is soon perceived. Dilute hydrocyanic acid is usually made by distilling potassium ferrocyanide (p. 214) with dilute sulphuric acid:

$$\underset{\text{Potassium ferrocyanide.}}{2K_4Fe(CN)_6} + 3H_2SO_4 = \underset{\text{Hydrocyanic acid.}}{6HCN} + \underset{\text{Potassium ferrous ferrocyanide.}}{K_2Fe''Fe(CN)_6} + 3K_2SO_4.$$

The solution slowly decomposes, on standing, into ammonium formate. The reaction is analogous to the formation of ammonium oxalate from cyanogen (p. 208):

$$HCN + 2H_2O = \underset{\text{Ammonium formate.}}{H.CO.ONH_4}.$$

EXPT. 106.—**Preparation of Hydrocyanic acid.**—As the acid vapours are excessively poisonous, it is desirable to conduct the following operation in a fume cupboard. Ten parts of coarsely-

powdered potassium ferrocyanide are placed in a retort, and 7 parts of concentrated sulphuric acid, previously diluted with from 10–20 parts of water, are added. The retort is connected with a well-cooled condenser and receiver. On distilling the mixture, aqueous hydrocyanic collects in the receiver.

The pure anhydrous acid is prepared by distilling a mixture of powdered potassium cyanide and moderately strong sulphuric acid and passing the vapour, which is evolved, through U-tubes containing solid calcium chloride to remove the water. The dry hydrocyanic acid vapour is then led into a U-tube surrounded by ice, where it condenses to a colourless liquid.

Properties of Hydrocyanic acid.—Pure hydrocyanic acid boils at 26° and solidifies at −14°. It is inflammable, and burns with a violet flame. It is excessively poisonous, even in the minutest quantity, and the greatest care should be taken in preparing and in using it.

Pure hydrocyanic acid is rapidly decomposed by strong hydrochloric acid with a considerable rise of temperature, first into formamide, and finally into formic acid and ammonium chloride:

$$\underset{\text{Hydrocyanic acid.}}{HCN} + H_2O = \underset{\text{Formamide.}}{HCO.NH_2}.$$

$$HCO.NH_2 + H_2O + HCl = \underset{\text{Formic acid.}}{H.CO.OH} + NH_4Cl.$$

Strong sulphuric acid probably effects the same change, but as it decomposes formic acid at the same time into carbon monoxide (p. 74), no formic acid is actually produced. This explains why carbon monoxide alone is formed when either potassium ferrocyanide or potassium cyanide is heated with strong sulphuric acid.

As hydrocyanic acid yields formamide on hydrolysis, so the reverse process may be effected by removing the elements of water from formamide.

On distilling formamide with phosphorus pentoxide, hydrocyanic acid is produced:

$$HCONH_2 - H_2O = HCN.$$

When an alcoholic solution of hydrocyanic acid is reduced with metallic sodium, methylamine is formed, just as methyl cyanide is converted into ethylamine (p. 205):

$$HCN + 2H_2 = \underset{\text{Methylamine.}}{CH_3.NH_2}.$$

The Metallic cyanides.—Potassium cyanide, KCN, and sodium cyanide, NaCN, are two of the most important salts of hydrocyanic acid. Potassium cyanide is formed by fusing potassium ferrocyanide alone,

$$1.\quad K_4Fe(CN)_6 = \underset{\substack{\text{Potassium}\\\text{cyanide.}}}{4KCN} + FeC_2 + N_2,$$

but is not used commercially. The large quantity of cyanide demanded for the extraction of gold from gold quartz by the MacArthur-Forrest process (p. 213) has led to the discovery of new and cheaper methods. When metallic sodium is heated with sodium ferrocyanide, obtained in the coal-gas manufacture, sodium cyanide is formed, and the whole of the cyanogen is obtained as cyanide:

$$\underset{\substack{\text{Sodium}\\\text{ferrocyanide.}}}{Na_4Fe(CN)_6} + Na_2 = 6NaCN + Fe.$$

The fused mass is then filtered from the finely-divided iron. Another important method is to pass ammonia gas over a heated or fused mixture of potassium carbonate and charcoal.

$$2NH_3 + K_2CO_3 + C = 2KCN + 3H_2O.$$

About 10,000 tons of cyanide are produced annually, of which about one-third is used in the Transvaal for gold extraction.

In addition to the application of potassium and sodium cyanides to gold extraction, these salts are employed in the preparation of solutions of gold and silver for electroplating. The cyanides of these metals form soluble **double salts** with potassium cyanide (p. 212). The alkali cyanides are very soluble in water, and the solutions undergo gradual decomposition. The action goes on more rapidly on boiling, ammonia being evolved and formates of the alkalis produced. Potassium and sodium cyanide are readily decomposed by the inorganic and organic

acids (and even by so weak an acid as carbonic acid) giving off hydrocyanic acid. The smell which potassium cyanide emits, when exposed to the air, is attributed to the action of carbon dioxide. Like hydrocyanic acid, the alkali cyanides are strong poisons.

Detection of Hydrocyanic acid and Cyanides.—Owing to the poisonous character of hydrocyanic acid and the soluble cyanides, the detection of the presence of these substances is a matter of importance. The volatility and peculiar smell of hydrocyanic acid render its separation and detection a comparatively simple matter. If nitric acid is added to a soluble cyanide and warmed, hydrocyanic acid is evolved. A drop of silver nitrate solution on a watch-glass, or glass rod, in contact with the vapour becomes turbid from the formation of silver cyanide. In the same way a drop of ammonium sulphide in contact with hydrocyanic acid vapour is converted into ammonium sulphocyanide, NH_4CNS. If the liquid is somewhat concentrated by warming and acidified with dilute hydrochloric acid, a blood-red stain is produced on the addition of a drop of ferric chloride. A common method of detecting hydrocyanic acid is to boil the liquid, which is first made alkaline with potash, with a few drops of ferrous sulphate and a drop of ferric chloride solution. On acidifying the solution, a precipitate of Prussian blue is formed. If the cyanide is mixed with other substances which would interfere with the reaction, it is first separated by distilling the mixture with the addition of a little non-volatile organic acid like tartaric acid. The distillate which contains the hydrocyanic acid is then submitted to the above tests.

The Double cyanides.—When a solution of potassium or sodium cyanide is added to the solution of a metallic salt, the metal (with the exception of the alkalis, alkaline earths, and mercury, which form soluble cyanides) is precipitated in the form of the insoluble cyanide. A further addition of potassium cyanide produces a solution of the metallic cyanide. A **double cyanide** is formed. If a mineral acid is now added to the solution hydrocyanic acid is evolved, and the insoluble cyanide of the metal is reprecipitated. In the case of silver, the addition of potassium cyanide to a solution of silver nitrate produces a precipitate of silver cyanide, AgCN, very similar to silver chloride in appearance, which redissolves on the further addition

of potassium cyanide, with the formation of a double cyanide AgCN.KCN. If nitric acid is now added, silver cyanide is reprecipitated, and hydrocyanic acid is evolved:

$$\underset{\text{Potassium silver cyanide.}}{AgCN.KCN} + HNO_3 = \underset{\text{Silver cyanide.}}{AgCN} + HCN + KNO_3.$$

In the extraction of gold, which occurs in a fine state of division in gold-bearing rocks, and in residues or tailings, a very dilute solution of potassium or sodium cyanide is used in presence of atmospheric oxygen, or other oxidising agent:

$$4KCN + 2Au + H_2O + O = 2KAu(CN)_2 + 2KOH.$$

The gold is then deposited from the solution by electrolysis or by the addition of metallic zinc:

$$2KAu(CN)_2 + Zn = K_2Zn(CN)_4 + 2Au.$$

Nearly 2 million ounces of gold are extracted by this process annually.

There is another class of double cyanides in which the metallic cyanide of the heavy metal is not precipitated from solution by a mineral acid. The formation and properties of this class of double cyanides may be illustrated by the following experiment.

EXPT. 107.—Make a fresh solution of ferrous sulphate and add a strong potassium cyanide solution until there is no further brown precipitate of cyanide of iron; boil and filter if necessary. A yellow solution is obtained, which, after cooling, is divided into two portions. If dilute hydrochloric acid is added to one portion, there is no precipitate of the original cyanide. If strong hydrochloric acid is added to the second portion, a white precipitate is thrown down if the solution is not too dilute. The yellow solution contains potassium ferrocyanide, and the addition of strong hydrochloric acid to the second portion precipitates hydroferrocyanic acid. The reactions which occur are expressed as follows:

1. $2KCN + FeSO_4 = \underset{\text{Ferrous cyanide.}}{Fe(CN)_2} + K_2SO_4.$
2. $Fe(CN)_2 + 4KCN = \underset{\text{Potassium ferrocyanide.}}{K_4Fe(CN)_6}.$
3. $K_4Fe(CN)_6 + 4HCl = \underset{\text{Hydroferrocyanic acid.}}{H_4Fe(CN)_6} + 4KCl.$

It therefore appears that in the second class of double cyanides the metallic cyanide forms an integral part of the acid. Hydroferrocyanic acid, $H_4Fe(CN)_6$, contains the acid radical or negative ion[1] **ferrocyanogen**, $Fe(CN)_6$. Hydroferrocyanic acid is a strong acid, and forms a series of salts, some of which, like the zinc (white), copper (red), and ferric (Prussian blue) salts are insoluble, and have a characteristic colour. They are obtained by adding a solution of a salt of the particular metal to a solution of potassium ferrocyanide. The most important salts are potassium and sodium ferrocyanides.

Potassium ferrocyanide (Yellow prussiate of potash), $K_4Fe(CN)_6+3H_2O$, is the starting-point in the preparation of nearly all the cyanogen compounds. Potassium ferrocyanide was formerly manufactured by fusing in an iron pot nitrogenous animal refuse, such as horns, hoofs, blood, leather scraps, etc., with potassium carbonate. The mass is kept stirred during the operation, and, after cooling, is extracted with water. On evaporation, large tabular yellow crystals of potassium ferrocyanide are deposited. A satisfactory explanation of the reaction has not yet been offered.

The sodium salt is now obtained almost exclusively from coal gas. The cyanogen derived from the coal, probably in the form of hydrocyanic acid, is absorbed by alkaline ferrous hydrate before passing to the purifiers, and is converted into **sodium ferrocyanide :**

$$Na_4Fe(CN)_6 + 10H_2O.$$

In other gas-works the cyanogen passes to the iron oxide of the "purifiers," and is converted into insoluble iron ferrocyanide. Some thiocyanate is also formed. The spent oxide is boiled with lime, and the soluble calcium ferrocyanide, which is formed, is extracted and converted into the sodium or potassium salt by treatment with an alkaline carbonate.

Reactions of Ferrocyanides.—When heated, potassium ferrocyanide first loses its water of crystallisation and becomes colourless; it then blackens and fuses, forming potassium cyanide and iron carbide (p. 211). Ferric salts added to a

[1] *Vide* J. Walker, *Introduction to Physical Chemistry*, Chap. xxvi. (Macmillan).

solution of the ferrocyanide give a precipitate of ferric ferrocyanide or Prussian blue:

$$Fe'''_4[Fe'''CN)_6]_3.$$
Ferric ferrocyanide, or Prussian blue.

When chlorine is passed into a solution of potassium ferrocyanide, the latter turns a deep red, and on evaporation red crystals of **potassium ferricyanide,** or **red prussiate of potash,** $K_3Fe(CN)_6$, are deposited:

$$2K_4Fe(CN)_6 + Cl_2 = 2K_3Fe(CN)_6 + 2KCl.$$
Potassium ferricyanide.

EXPT. 108.—The above reaction also takes place on the addition of bromine. Add bromine water in excess to a solution of potassium ferrocyanide and boil off the excess of bromine. The solution may be evaporated, when red crystals of the ferricyanide are obtained. If a drop of ferric chloride is added to the solution of the ferricyanide, no precipitate of Prussian blue is formed; but the solution turns dark brown. The addition of a ferrous salt throws down a blue precipitate, known as **Turnbull's blue,** or ferrous ferricyanide, $Fe''_3[Fe(CN)_6]_2$.

Potassium ferricyanide is occasionally used in alkaline solution as a mild oxidising agent. It decomposes the alkali and liberates oxygen, forming at the same time potassium ferrocyanide, according to the following equation:

$$2K_3Fe(CN)_6 + 2KOH = 2K_4Fe(CN)_6 + H_2O + O.$$
Potassium ferricyanide. Potassium ferrocyanide.

When potassium ferrocyanide is heated with moderately strong nitric acid, and then neutralised with caustic soda, **sodium nitroprusside,** $Na_2NOFe(CN)_5 + 2H_2O$, crystallises out on evaporation in the form of ruby red crystals. Sodium nitroprusside solution is used as a test for sulphur. The sulphur, when present in the form of a soluble sulphide in alkaline solution, produces a deep violet coloration on the addition of sodium nitroprusside solution.

EXPT. 109.—**Test for sulphur in organic compounds.**—Heat a fragment of cheese with a small piece of sodium in a test-tube. When the bottom of the tube is red-hot, place it in a small beaker of water, as described in the test for nitrogen (Expt. 97, p. 198). Filter

the liquid and add a few drops of sodium nitroprusside solution prepared from the crystals.

Cyanic and Cyanuric acids.—Cyanuric acid, $C_3N_3O_3H_3 + 2H_2O$, is obtained by a variety of reactions, such as heating urea (p. 222), alone or in presence of chlorine:

$$\underset{\text{Urea.}}{3CON_2H_4} = \underset{\text{Cyanuric acid.}}{C_3N_3O_3H_3} + 3NH_3.$$

$$6CON_2H_4 + 3Cl_2 = 2C_3N_3O_3H_3 + 4NH_4Cl + 2HCl + N_2,$$

or it may be obtained by heating in a sealed tube a solution of carbonyl chloride (in an inert solvent like benzene) with ammonia:

$$3COCl_2 + 3NH_3 = C_3N_3O_3H_3 + 6HCl.$$

Cyanuric acid is a very stable substance and dissolves unchanged in strong sulphuric acid. When distilled and the vapours cooled in a freezing mixture, it is converted into liquid **cyanic acid,** CNOH, which is an extremely unstable substance; for, when warmed to the ordinary temperature, it polymerises with explosive violence, and forms a compound known as **cyamelide,** which undergoes slow transformation into cyanuric acid.

Potassium cyanate, CNOK, is obtained by oxidising potassium cyanide. This may be effected by fusing the cyanide with some reducible metallic oxide, like lead or manganese peroxide, or by adding permanganate solution to a solution of potassium cyanide. The use of potassium cyanide as a reducing agent for metallic oxides depends upon this reaction:

$$KCN + O = KOCN.$$

Ammonium Cyanate, $CNO(NH_4)$, may be prepared by bringing together ethereal solutions of ammonia and cyanic acid, cooled in a freezing mixture. It forms a white crystalline powder. If the solid (or a solution in water or alcohol) is heated, an "intramolecular" rearrangement, or change in the positions of the atoms, occurs, and the ammonium cyanate is transformed into urea. The nature of this change will be seen from the equation (p. 217). In the preparation of urea from potassium cyanate, it is only necessary to add ammonium sulphate to the solution of the cyanate in water and evaporate the mixture to

dryness. The ammonium cyanate, which is first formed, is thereby converted into urea, which may be extracted from the dried mass with alcohol. The alcohol dissolves the urea, but not the potassium sulphate. The urea crystallises from the alcoholic solution:

$$2CNOK + (NH_4)_2SO_4 = 2\underset{\text{Ammonium cyanate.}}{CNO.NH_4} + K_2SO_4.$$

$$CNO.NH_4 = \underset{\text{Urea.}}{CO(NH_2)_2}.$$

EXPT. 110.—**Preparation of Potassium cyanate and Urea.**—Heat 50 grams of pure potassium cyanide in powder in a small iron dish over a large Bunsen burner, and, without waiting for the cyanide to fuse, add gradually 140 grams of red lead. The addition of the red lead produces sufficient heat to melt the contents of the dish. When the red lead has been added, and the mixture fuses quietly without effervescence, pour it out on to a cold slab or iron tray:

$$4KCN + Pb_3O_4 = 4CNOK + 3Pb.$$

Powder the mass, when cold, and separate the potassium cyanate from lead and other impurities by leaving the mass in contact with about 200 c.c. of water for an hour. The solution now contains the potassium cyanate. Filter, and add to the filtrate 50 grams of ammonium sulphate dissolved in water, and evaporate the mixture to dryness on the water-bath. Boil with about 50 c.c. of methylated spirit on the water-bath, and filter into a crystallising dish. Long prismatic crystals of urea deposit on cooling.

Mercury fulminate, $C_2N_2O_2Hg + \frac{1}{2}H_2O$, is formed by the action of alcohol on a solution of mercuric nitrate in nitric acid. Its structure is represented as the mercury salt of carbyloxime, and it is therefore isomeric with mercury cyanate:

$$\underset{\text{Mercury fulminate.}}{(C{:}NO)_2Hg}.$$

Esters of the Cyanogen acids.—Hydrocyanic, cyanic, and cyanuric acids form a series of esters. Each acid, however, gives rise to, not one, but two isomeric esters, the existence of which is accounted for by differences of structure, which will be presently discussed.

Nomenclature of the Cyanogen esters.—It will be con-

venient to give at once the names and structural formulæ of the series of esters above referred to, taking the methyl esters by way of illustration. From hydrocyanic acid are derived **methyl cyanide** and **methyl isocyanide.**

As the alkyl cyanides, like hydrocyanic acid itself, are converted on hydrolysis into the fatty acids (p. 210), they are sometimes designated as the **nitriles** of the corresponding acids.

Hydrocyanic acid is the nitrile of formic acid, methyl cyanide of acetic acid, ethyl cyanide of propionic acid, etc.



Hydrogen cyanide, or Formonitrile. | Methyl cyanide, or Acetonitrile. | Ethyl cyanide, or Propionitrile.

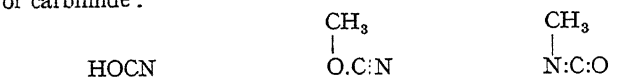
The alkyl isocyanides, which are converted into alkylamines on hydrolysis, are also termed alkyl **carbamines,** or **carbylamines.**

Methyl isocyanide is also known as methyl carbamine:



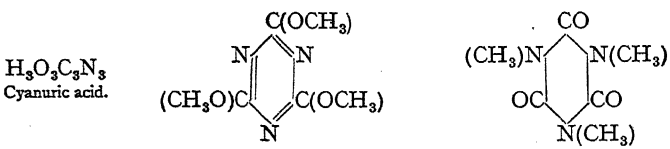
Methyl isocyanide, or Methyl carbamine.

From cyanic acid are derived methyl cyanate and isocyanate or carbimide:



HOCN Cyanic acid. | Methyl cyanate. | Methyl isocyanate. Methyl carbimide.

From cyanuric acid, in the same way, methyl cyanurate and isocyanurate are derived, to which the following structural formulæ have been assigned



$H_3O_3C_3N_3$ Cyanuric acid. | Methyl cyanurate. | Methyl isocyanurate.

Attention is directed to the fact that all the iso-esters contain the carbon of *the alkyl group linked to nitrogen.*

The Alkyl cyanides or Nitriles.—Certain methods of preparation of the cyanides have already been described. The alkyl cyanides may be obtained by the action of potassium cyanide in aqueous-alcoholic solution upon the alkyl iodide (p. 78):

$$CH_3I+KCN=CH_3CN+KI,$$

or by distilling the amides with phosphorus pentoxide (p. 198).

The lower members of the series are colourless liquids with a strong but not unpleasant smell. They are soluble to some extent in water. The higher members are less soluble in water, and are solid, crystalline substances.

The most important characteristics of the alkyl cyanides are their rapid conversion into fatty acids on hydrolysis with mineral acids or alkalis, and their reduction to the corresponding amine by the action of sodium on the alcoholic solution of the cyanide. Methyl cyanide is converted into ethylamine in the same way that hydrocyanic acid is reduced to methylamine (p. 211):

$$CH_3C{:}N+2H_2=\underset{\text{Ethylamine.}}{CH_3.CH_2.NH_2}.$$

The formation of acids and amines from the cyanides clearly indicates that the carbon of the cyanogen group is directly linked to the carbon of the alkyl group.

The Alkyl isocyanides, or **Carbamines,** are isomeric with the cyanides. They are formed by the action of chloroform and alcoholic potash on the primary amines (p. 203).

Methyl isocyanide is prepared by distilling a mixture of methylamine, chloroform, and alcoholic potash:

$$CH_3N{:}H_2+C{:}HCl_3+3KOH=\underset{\substack{\text{Methyl}\\\text{isocyanide.}}}{CH_3NC}+3KCl+3H_2O.$$

The isocyanides are liquids with an intolerable smell. They are hydrolysed by hydrochloric acid into an amine and formic acid, the reaction probably occurring in two stages:

$$CH_3NC+H_2O=\underset{\text{Methyl formamide.}}{CH_3NH.CHO}$$

$$CH_3NH.CHO+H_2O=\underset{\text{Methylamine.}}{CH_3NH_2}+\underset{\text{Formic acid.}}{CH_2O_2}.$$

This reaction also indicates the attachment of the alkyl group to nitrogen and thus determines the structure of the isocyanides.

The Alkyl isocyanates (Carbimides) were originally prepared by Wurtz (1854) by distilling an alkyl potassium sulphate with potassium cyanate:

$$CH_3OSO_3K + KNCO = CH_3N{:}CO + K_2SO_4.$$

Potassium methyl sulphate. Methyl isocyanate.

A more convenient method is to heat a mixture of silver cyanate and alkyl iodide:

$$CH_3I + AgNCO = CH_3N{:}CO + AgI.$$

The isocyanic esters are volatile liquids with a powerful and suffocating odour. Like the cyanic esters, they polymerise on standing, forming isocyanuric esters. The most interesting property of the isocyanic esters is their conversion into amines on boiling with alkalis (p. 200):

$$CH_3N{:}CO + H_2O = CH_3NH_2 + CO_2.$$

Methyl isocyanate. Methylamine.

The Mustard oils, or **Alkyl isothiocyanates,** so called from the fact that black mustard seed contains one of these compounds in the form of a glucoside (p. 209), are most easily obtained by the action of carbon disulphide on the primary amines. The compound first formed is the alkylamine salt of an alkyl thiocarbamate:

$$CS_2 + 2NH_2CH_3 = CS\begin{matrix}\diagup NHCH_3 \\ \diagdown SH.NH_2.CH_3.\end{matrix}$$

Methylamine methyl thiocarbamate.

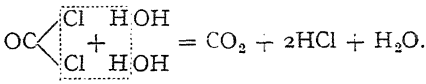
If this compound is now treated with mercuric chloride, hydrogen sulphide is removed, and the thiocarbamate splits up into the mustard oil and primary amine:

$$SC\begin{matrix}\diagup NHCH_3 \\ \diagdown SH\ NH_2.CH_3\end{matrix} = SC{:}NCH_3 + NH_2.CH_3 + H_2S.$$

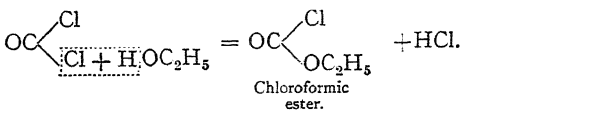
Methyl mustard oil.

The above reaction is occasionally used as a test for primary amines (p. 202).

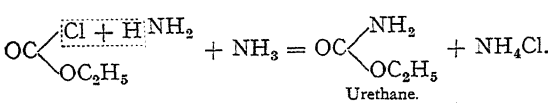
Carbonyl Chloride.—Carbonyl chloride, or phosgene, which is obtained by the direct union of carbon monoxide and chlorine in presence of a catalyst (charcoal), has the properties of an acid chloride, and may be regarded as the acid chloride of carbonic acid. The gas fumes in moist air, decomposing into hydrochloric acid and carbon dioxide:



It is also decomposed by alcohol, and gives chloroformic ester according to the following equation:

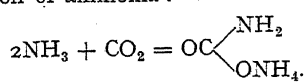


Urethane, Ethyl carbamate, $NH_2.CO.OC_2H_5$, is the product formed by the action of ammonia on chloroformic ester, and is used as a hypnotic:



A variety of similar hypnotics are produced by replacing the amino-group with substituted amino-groups, ethoxy-groups and by other alkoxy-radicals. **Hedonal,** $NH_2.CO_2C_5H_{11}$, is an example. Hedonal is also used as an anæsthetic.

Urethane is the ethyl ester of carbamic acid. The acid itself is unknown in the free state, but the ammonium salt is a common constituent of commercial ammonium carbonate. Ammonium carbamate is readily obtained by passing carbon dioxide into an alcoholic solution of ammonia:



EXPT. III.—Pass ammonia gas into ethyl alcohol until the alcohol is saturated, then bubble carbon dioxide through the liquid. Ammonium carbamate is precipitated in the form of a white crystalline powder.

Urea, Carbamide, $CO(NH_2)_2$.—When ammonia is added to carbonyl chloride, urea is formed, just as acetamide is obtained when ammonia acts upon acetyl chloride (p. 63):

$$CH_3.COCl + HNH_2 + NH_3 = CH_3.CONH_2 + NH_4Cl.$$

Acetamide.

$$CO\begin{matrix}Cl\ H\ NH_2\\ +\\ Cl\ H\ NH_2\end{matrix} + 2NH_3 = OC\begin{matrix}NH_2\\ \\ NH_2\end{matrix} + 2NH_4Cl.$$

Urea.

This reaction determines the constitution of urea, as the amide of carbonic acid. Hence the name carbonic amide, or shortly **carbamide**, which is synonymous with urea.

That the substance is an amide is further seen from its behaviour with boiling caustic alkalis, which decompose it into ammonia and a salt of carbonic acid (p. 198):

$$OC\begin{matrix}NH_2\\ \\ NH_2\end{matrix} + 2NaOH = Na_2CO_3 + 2NH_3.$$

The presence of amino-groups is also shown by the action of nitrous acid, which liberates nitrogen; at the same time carbon dioxide is evolved:

$$\begin{matrix}HO\ N\ O\\ +\\ CO\begin{matrix}N\ H_2\\ \\ N\ H_2\end{matrix}\\ +\\ HO\ N\ O\end{matrix} = CO_2 + H_2O + 2N_2 + 2H_2O.$$

EXPT. 112.—Add to a solution of urea in water, a little sodium nitrite solution and a few drops of hydrochloric acid. Effervescence occurs and nitrogen and carbon dioxide are evolved.

The usual method for obtaining urea has already been described (p. 216). It is a colourless substance with crystallises in long prisms melting at 132°. It is very soluble in water and in hot alcohol. When heated, it decomposes into ammonia, biuret and cyanuric acid (p. 216).

The chief interest attaching to urea is its presence in normal

human urine, about 30 grams being excreted daily. Urea may be regarded as the final decomposition product of the waste nitrogenous materials of the body. It is obtained from urine by concentration and extraction with alcohol, which dissolves out the urea. The alcoholic extract is allowed to evaporate and the urea then crystallises.

When urine is exposed to the air, fermentation sets in, the urea being converted by the enzyme, *urease*, into ammonium carbonate:

$$CO(NH_2)_2 + 2H_2O = (NH_4)_2CO_3.$$

Detection and estimation of Urea.—The presence of urea may be detected by a variety of reactions, which are described in the following experiments:—

EXPT. 113.—1. Heat a few crystals of urea over a very small flame until they melt and slowly evolve bubbles of ammonia gas. Continue to heat for a minute or two, then cool and add a few drops of water, a drop or two of copper sulphate solution, and finally caustic soda solution, until a clear solution is obtained. A violet, or pink, solution is produced, which is a compound of biuret with copper. The formation of biuret from urea takes place according to the following equation:

$$\underset{\text{Urea.}}{NH_2.CO.NH_2} + \underset{\text{Urea.}}{NH_2.CO.NH_2} = \underset{\text{Biuret.}}{NH_2.CO.NH.CO.NH_2} + NH_3.$$

Two molecules of urea combine with the elimination of one molecule of ammonia.

2. Add to a solution of urea a few drops of a neutral solution of mercuric nitrate. A white, curdy precipitate is thrown down, which is a basic compound of mercuric nitrate and urea:

$$[CO(NH_2)_2]_2.Hg(NO_3)_2.3HgO.$$

3. Add to a strong solution of urea in water a few drops of strong nitric acid, and to another portion a strong solution of oxalic acid. In one case urea nitrate and, in the other, urea oxalate is precipitated in crystals which have a characteristic appearance under the microscope:

$$\underset{\text{Urea nitrate.}}{CO(NH_2)_2.HNO_3} \qquad \underset{\text{Urea oxalate.}}{[CO(NH_2)_2]_2C_2H_2O_4 + H_2O.}$$

4. Add to a solution of urea a few drops of an alkaline solution of sodium hypochlorite or hypobromite. Effervescence occurs,

and free nitrogen is evolved, the alkali retaining the carbon dioxide which is liberated at the same time:

$$\begin{array}{l} H_2N- \\ + \\ Na\,O\,Cl \end{array} \quad \begin{array}{l} CO- \\ + \\ Na\,O\,Cl \end{array} \quad \begin{array}{l} NH_2 \\ + \\ Na\,O\,Cl \end{array} = 3NaCl + 2H_2O + CO_2 + N_2.$$

Estimation of Urea.—This reaction is utilised for the quantitative estimation of urea in urine. It may be performed by the aid of **Lunge's nitrometer** (Fig. 56) or other convenient apparatus. A solution of sodium hypobromite is prepared by dissolving 100 grams of caustic soda in 250 c.c. of water and adding 25 c.c. of bromine.

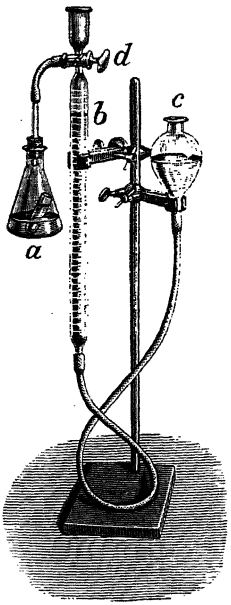


FIG. 56.—Lunge's Nitrometer for the estimation of urea.

25 c.c. of this solution are introduced into the flask, *a*, together with a small tube containing 5 c.c. of urine. The graduated vessel, *b*, is filled with water by raising the reservoir, *c*. The pressure in the flask is adjusted by turning the three-way tap, *d*, so that the vessel is for a moment in communication with the air. The tap is then turned so that a connection is made between the flask and the graduated tube, and the small tube containing the urine is then allowed to drop into the hypobromite solution. Nitrogen is evolved, and the liquid in *b* descends. When gas ceases to be evolved, the pressure in the graduated tube is adjusted by means of the reservoir, and the volume of gas is read off. The volume of gas corresponding to the urea present is always about 7 per cent. below the theoretical amount, and a correction to this extent must be introduced. In analysing urine it is customary to estimate, in addition to the urea, the total nitrogen by Kjeldahl's method (p. 239).

QUESTIONS ON CHAPTER XVII

1. How is cyanogen most easily prepared ? Compare cyanogen and chlorine.

2. What products are obtained by the hydrolysis of cyanogen, hydrocyanic acid, methyl cyanide, methyl isocyanide, and methyl isocyanate ? What reagent is required in each case ?

3. Describe a method for preparing potassium cyanide and sodium cyanide. In what manner has atmospheric nitrogen been utilised in the preparation of cyanides ?

4. How is hydrocyanic acid detected ? Describe a quantitative method for analysing potassium cyanide.

5. What is meant by a *double cyanide* ? How may the two classes of double cyanides be distinguished ?

6. How is yellow prussiate of potash converted into the red prussiate, and *vice versa* ?

7. Describe and explain the formation of urea from potassium cyanide.

8. How may the following compounds be obtained from potassium ferrocyanide : carbon monoxide, hydrocyanic acid, potassium cyanide, hydroferrocyanic acid, and cyanogen ?

9. What is meant by the term *mustard oil* ? How are the mustard oils obtained ?

10. Discuss the structure of isomeric compounds of the formula C_3H_5N (cyanide and isocyanide).

11. Give an account of the preparation and properties of cyanogen gas. Why is cyanogen considered to be analogous to chlorine, and in what respects does it differ from chlorine ?

12. How is potassium ferrocyanide manufactured ? How would you prepare from potassium ferrocyanide (*a*) a dilute solution of prussic acid, (*b*) urea, (*c*) carbon monoxide ?

13. How do you account for the different action of strong and dilute sulphuric acid on potassium ferrocyanide ?

14. Starting from mercury and potassium ferrocyanide, how would you prepare mercuric cyanide ? Describe its properties and compare them with those of potassium cyanide.

15. Describe the mode of preparation and properties of cyanic and cyanuric acids. Point out the relation between the two substances.

16. Explain by examples the isomerism of carbimides and nitriles. How is each class of bodies prepared ? How can the formulæ ascribed to each be proved to be correct ?

17. What is a nitrile? How can it be obtained from an ammonium salt, and what transformation does it undergo when hydrolysed and when reduced by nascent hydrogen?

18. Why is urea called carbamide? Mention two experiments which support this view of its constitution. Calculate the quantity of urea in a specimen which gave the following results on analysis: 0·0884 gram gave 32·8 c.c. of moist nitrogen at 19° and 753 mm.

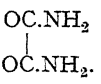
19. How would you proceed in order to prepare urea from (1) carbon monoxide, (2) potassium cyanide? Explain the changes which are induced by (1) heat, (2) nitrous acid, (3) aqueous alkalis, (4) nitric acid.

20. How is urea identified? What volume of nitrogen measured at 15° and 740 mm. should be evolved from 0·5 gram of urea?

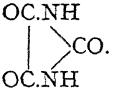
CHAPTER XVIII

THE UREIDES

THE **ureides** are compounds of urea with acids and belong to the class of amides. The ureide of oxalic acid or oxalyl urea may be compared with oxamide:

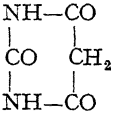


Amide of Oxalic acid, or Oxamide.

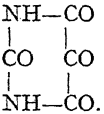


Ureide of Oxalic acid, Oxalyl urea, or Parabanic acid.

A large number of ureides of the dibasic acids are known, of which the following are examples:



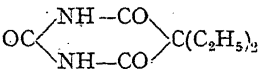
Malonyl urea, or Barbituric acid.



Mesoxalyl urea, or Alloxan.

Certain derivatives of malonyl urea have received important applications in medicine.

Veronal, the diethyl derivative, is a valuable hypnotic:



Veronal.

The dipropyl derivative, or **propional,** is used for the same purpose.

The most important of the more complex ureides, known as diureides, is uric acid.

Uric acid, $C_5H_4N_4O_3$.—The composition of chalk stones and urinary calculi attracted the attention of physicians and alchemists at a very early period, and they speculated freely on their origin, submitting them to the usual process of dry distillation without eliciting much information. It is interesting to learn that Paracelsus looked upon them as deposits originating in the same manner as the lees, or tartar of wine. The discovery of uric acid, or, as it was then termed, **lithic acid**, in urinary concretions is due to Scheele, who in 1776 isolated the acid and observed the red colour which it produces with nitric acid on evaporation. Prout subsequently noticed the change to violet which ammonia produces, now known as the **murexide** test. It is the principal test for uric acid.

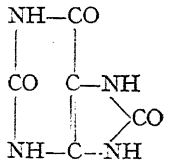
EXPT. 114.—**Test for Uric acid.**—Evaporate a minute quantity of uric acid with a few drops of dilute nitric acid to dryness on the water-bath, then add to the red residue, when cold, a few drops of ammonia. A deep violet coloration is produced.

Uric acid is the chief constituent of the excreta of birds and reptiles. The excrement of snakes is nearly pure ammonium urate, $C_5H_3N_4O_3(NH_4)$. Guano contains a considerable quantity of uric acid together with guanine, which will be described later. The amount excreted by mammals is very small, not more than 0·2–1 gram being found in human urine in 24 hours. It is usually present in the urine as the acid ammonium salt; in the blood and calculi of gouty patients as the acid sodium salt $C_5H_3N_4O_3Na$. It is precipitated from urine by adding 2 to 3 per cent. of strong hydrochloric acid and allowing the liquid to stand for a few days. Uric acid is usually obtained from snake or fowls' excrement or from guano. The material is boiled with caustic soda or potash until ammonia ceases to be evolved. The uric acid dissolves as the sodium salt, and the liquid is then filtered and the uric acid precipitated by the addition of a mineral acid.

Uric acid and the urates have a characteristic crystalline appearance, which is readily recognised under the microscope. Uric acid is very slightly soluble in water, but dissolves in caustic

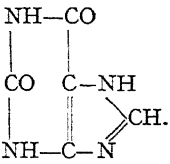
alkalis and in strong sulphuric acid without decomposition, It decomposes on dry distillation, without fusion, into ammonia. cyanuric acid, and urea. On oxidation it breaks up into urea and alloxan.

The following structural formula has, for various reasons, been adopted :



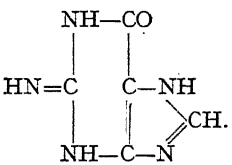
Formula of Uric acid.

Xanthine, $C_5H_4N_4O_2$, is common to the vegetable and animal kingdom. It is present in extract of meat, in lupine seedlings, in malt, and in tea. It is closely related to uric acid ; for though it contains one atom of oxygen less than uric acid, it yields the same products on oxidation, viz. alloxan and urea. It has therefore received the following structural formula :



Xanthine.

Guanine, $C_5H_5N_5O$, is obtained from guano by first extracting with boiling milk of lime. The residue is then heated with sodium carbonate, which dissolves the guanine. After precipitation with acetic acid, the guanine is purified by crystallising the hydrochloride from hot, dilute hydrochloric acid. On oxidation it yields guanidine, $HN{:}C(NH_2)_2$, and parabanic acid. With nitrous acid it is converted into xanthine.



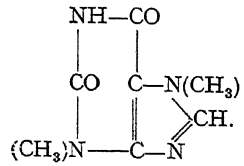
Guanine.

Theobromine, Dimethylxanthine, $C_7H_8N_4O_2$, is present in cocoa beans (*Theobroma cacao*) to the extent of 1–2 per cent. It has been synthesised from xanthine by acting with methyl iodide on the silver compound of xanthine.

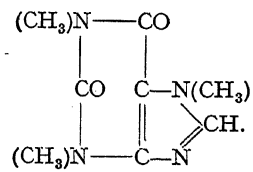
Caffeine, Theine, Trimethylxanthine, $C_8H_{10}N_4O_2$, is present in coffee and tea. Coffee beans contain about 1 per cent., tea leaves from 1·5 to 2·5, or sometimes 3 per cent. of caffeine. It is readily prepared from tea.

EXPT. 115.—**Preparation of Caffeine from Tea.**—Digest 100 grams of tea with 500 c.c. of boiling water for a quarter of an hour, and filter through cloth into a basin placed over a ring burner, so that the liquid in the filter is kept hot. Moderately fine unsized cotton cloth is used, and is wetted and stretched on a wooden frame. Wash with a further 250 c.c. of boiling water. Add to the filtrate a solution of basic lead acetate (made by boiling acetate of lead solution with excess of litharge, and then filtering) until no more precipitate is formed. Filter hot through a large fluted filter from precipitated protein, and wash with water. To the boiling filtrate add dilute sulphuric acid until the lead is precipitated as sulphate. Filter or decant from the sulphate of lead, and concentrate the solution with the addition of animal charcoal to 250–300 c.c. Filter and extract the filtrate three times with small quantities (50 c.c.) of chloroform. Distil off the chloroform on the water-bath, and dissolve the residue in a small quantity of hot water. On allowing the solution to evaporate very slowly, long silky needles of caffeine separate, which may have a slightly yellow tint, in which case they should be drained, re-dissolved in water, and boiled with the addition of animal charcoal. The needles contain one molecule of water, which they lose at 100°, and melt at 234·5°. The yield is about 1·5 grams.

Caffeine has been synthesised from theobromine by forming the silver compound of the latter and acting upon it with methyl iodide. In this way a third methyl group is introduced into xanthine. The following are the structural formulæ of theobromine and caffeine:



Theobromine.
(Dimethyl xanthine.)



Caffeine.
(Trimethyl xanthine.)

QUESTIONS ON CHAPTER XVIII

1. Explain and illustrate by examples the meaning of the term ureide.

2. How do you obtain pure uric acid? What is the action of nitric acid upon uric acid?

3. Give the graphic formula for uric acid, and show how, by oxidation with nitric acid, it yields alloxan and urea.

4. What is the nature of the bodies included in the uric acid group? Give a short sketch of the more important of these.

5. How is caffeine usually obtained? Describe its preparation.

6. How do you account for the acid properties of uric acid?

7. Explain the relations of xanthine, theobromine, and caffeine.

CHAPTER XIX

THE AMINO-ACIDS AND THE PROTEINS

The **Amino-acids** derive their interest from their occurrence among the decomposition products of albuminoid substances or proteins (p. 235). The amino-derivatives of the fatty acids are acids in which one atom of hydrogen of the alkyl group is replaced by the amino (NH_2) group. They are consequently both amines and acids, the result being that they are neutral substances.

They are formed, as already explained, by the action of ammonia on the halogen derivatives of the fatty acids.

Glycine, Glycocoll, Amino-acetic acid, $CH_2(NH_2).CO.OH$.—This compound was originally prepared by boiling gelatine or glue with dilute sulphuric or hydrochloric acid, or caustic soda. It crystallises in large, four-sided prisms which have a sweet taste. Hence, it received the name of glycocoll (γλυκύς, sweet; κόλλα, glue) or gelatine-sugar. It is most conveniently prepared by mixing chloracetic acid and ammonia solution:

$$\underset{\text{Chloracetic acid.}}{\begin{matrix}CH_2Cl\\|\\CO.OH\end{matrix}} + 3NH_3 = \underset{\text{Glycine ammonia.}}{\begin{matrix}CH_2(NH_2)\\|\\CO.ONH_4\end{matrix}} + NH_4Cl.$$

EXPT. 116.—**Preparation of Glycine.**—Pour 600 c.c. of ammonia (sp. gr. 0·907) into a wide-necked flask and slowly run in from a tap-funnel, whilst stirring, 50 grams of chloracetic acid dissolved in 50 c.c of water. A mechanical stirrer is convenient for this purpose. Allow the solution to stand overnight, pour into a basin and then drive off the excess of ammonia by a current of steam whilst evaporating on the water-bath. When the ammonia has disap-

peared add copper carbonate in powder to the hot liquid until effervescence ceases. Filter and evaporate the blue solution until crystals of copper salt begin to separate. Cool and filter the blue needles of copper glycine. Evaporate the mother liquid to obtain a further quantity. Dissolve the copper salt in water and pass into the hot solution a current of hydrogen sulphide. Filter from the copper sulphide and evaporate the filtrate to a small bulk on the water-bath. The liquid left in a vacuum desiccator over sulphuric acid deposits colourless crystals of glycine.

Glycine exhibits the property of a primary amine in its behaviour with nitrous acid. The amino-group is replaced by hydroxyl, nitrogen is evolved, and glycollic acid is formed:

$$\begin{matrix}CH_2NH_2\\|\\COOH\end{matrix} + HNO_2 = \begin{matrix}CH_2(OH)\\|\\COOH\end{matrix} + N_2 + H_2O.$$

It differs from an amide inasmuch as it does not evolve ammonia when heated with a solution of caustic soda.

Derivatives of Glycine.—Hippuric Acid, or benzoyl glycine, is glycine in which a hydrogen atom of the amino-group is replaced by the aromatic acid radical *benzoyl* (p. 294). The formula of hippuric acid is:

$$\begin{matrix}CH_2.NH(CO.C_6H_5)\\|\\CO.OH\end{matrix}$$

Hippuric acid, or Benzoyl glycine.

It is found in the urine of herbivorous animals, and crystallises in long, white prisms, which readily decompose on boiling with strong hydrochloric acid into benzoic acid and glycine:

$$\begin{matrix}CH_2.NH\\|\\CO.OH\end{matrix}\quad\begin{matrix}CO.C_6H_5\\+\\H\quad OH\end{matrix} = \begin{matrix}CH_2.NH_2\\|\\CO.OH\end{matrix} + C_6H_5CO.OH.$$

Benzoic acid.

EXPT. 117.—Boil a few crystals of hippuric acid with strong hydrochloric acid. Cool and filter off the crystals of benzoic acid, add a slight excess of ammonia to the filtrate, and boil until the solution is neutral and the excess of ammonia driven off. The addition of a few drops of copper sulphate solution will produce the characteristic deep blue colour of copper glycine.

Sarcosine, Methyl glycine, $(CH_3NH)CH_2.CO_2H$, is obtained by boiling creatine (see below) with baryta solution. It may be prepared synthetically by the action of methylamine on chloracetic acid:

$$\begin{matrix} CH_2Cl \\ | \\ CO_2H \end{matrix} + H.NHCH_3 = \begin{matrix} CH_2.NHCH_3 \\ | \\ CO_2H \end{matrix} + HCl.$$

Creatine, Methylguanidine acetic acid, $C_4H_9N_3O_2$, is present in small quantity in the juice of meat together with sarcolactic acid. It is readily obtained by precipitating the albumin from meat extract with basic lead acetate. The liquid is filtered and the lead removed with hydrogen sulphide. On concentrating the filtrate on the water-bath, a brown, viscid liquid remains, from which, on cooling, creatine crystallises in long prisms. When boiled with baryta water creatine is hydrolysed, and yields urea and sarcosine:

$$\begin{matrix} & NH_2 & & & \\ & | & & & \\ HN:C & -N(CH_2).CH_2.CO_2H & = CO(NH_2)_2 & + (CH_3)HN.CH_2.CO_2H. \\ & \text{Creatine.} & \text{Urea.} & & \text{Sarcosine.} \\ +HO & H & & & \end{matrix}$$

Creatinine, $C_4H_7N_3O$, is the anhydride of creatine:

$$\begin{matrix} HN:C-N(CH_3).CH_2 \\ | \qquad\qquad | \\ NH\text{———}CO. \end{matrix}$$

Creatinine.

It is a normal constituent of urine, but the quantity is usually very small. It crystallises in colourless prisms, having a characteristic, lenticular form.

Among the better-known amino-acids, found among the decomposition products of proteins, are **Alanine,** or α-aminopropionic acid, $CH_3.CH(NH_2).CO_2H$, a product of the decomposition of silk, and **Leucine,** or α-amino-isobutyl acetic acid, $(CH_3)_2.CH.CH_2.CH(NH_2).CO.OH$, which is obtained, together with glycine and other substances, by the decomposition of gelatine, glue, and other proteins by boiling them with mineral acids or caustic alkalis. Leucine is also formed during the digestion of proteins by trypsin, an enzyme derived from the pancreas.

Asparagine, Aminosuccinamide, $CO_2H.CH(NH_2).CH_2.CO(NH_2)$, receives its name from having been first found in asparagus (1805).

but it is very widely distributed in the vegetable kingdom, and is present in the parts of the plant which afford a store of reserve material, such as bulbs, tubers, and seedlings. The dried seedlings of lupines contain 20–30 per cent. of asparagine. It yields aspartic acid on hydrolysis with caustic potash solution:

$$\begin{array}{l} CH(NH_2).CO_2H \\ | \\ CH_2.CO.NH_2 \\ + H\,O\,H \end{array} = \begin{array}{l} CH(NH_2).CO_2H \\ | \\ CH_2.CO_2H \end{array} + NH_3.$$

Asparagine. Aspartic acid.

Aspartic Acid, Aminosuccinic acid, $CO_2H.CH(NH_2).CH_2.CO_2H$, occurs in beet-root molasses, and is formed from proteins by the action of mineral acids. It is converted into malic acid by the action of nitrous acid. The reaction resembles the conversion of a primary amine into an alcohol, or of glycine into glycollic acid (p. 233).

THE PROTEINS

The term **albumin** or **protein** is given to certain colourless, amorphous substances composing the solid constituents of animal tissues, plant cells, and other products of animal and plant life. They are identified by certain reactions, which, however, are probably due to certain groups present in the molecule, rather than to the molecule as a whole. It is certain that many of the substances giving the reactions vary much in complexity as well as in chemical behaviour.

Reactions of the Proteins.—1. A solution of mercury in excess of nitric acid (Millon's reagent), added to a protein, gives a precipitate which turns red on heating.

2. A few drops of copper sulphate and an excess of caustic soda produce a violet colour, which becomes deeper in tint on boiling the solution (biuret reaction).

3. A violet coloration is produced by adding a few drops of glyoxalic acid (p. 175) and strong sulphuric acid (Adamkiewicz's reaction).

Composition of the Proteins.—The percentage composition of the proteins varies very little. The following represents the

minimum and maximum amounts in parts per hundred, found in different proteins :

C	50 —55
H	6·9— 7·3
N	15 —19
O	19 —24
S	0·3— 2·4

Although egg- and serum-albumin have been prepared in the crystalline form, from which it may be concluded that they are single substances, no trustworthy information as to the molecular weight is at present forthcoming. There is no doubt that even the simplest of the proteins consist of highly complex molecules about the structure of which little is known. They may be compared with the polysaccharose group of carbohydrates, which possess a complex structure and high molecular weight but readily break up into fragments of comparatively simple constitution. These simple constituents of the proteins, which are produced by the action of acids and alkalis, are, for the most part, amino-acids, glycine (p. 232), alanine (p. 234), leucine (p. 234), aspartic acid (p. 235), and the guanidine acids, like creatine (p. 234) and arginine, or guanidine α-aminovaleric acid :

$$\begin{array}{l} \quad\quad NH_2 \\ \quad\quad | \\ HN{:}C{-}NH.CH_2.CH_2.CH_2.CH(NH_2).CO_2H. \end{array}$$

Arginine.

The latter substance is one of the first products of decomposition of the simplest proteins, or **protamines,** found in the spermatozoa (milt) of fishes. Among the more complex constituents of the protein molecule composing the nucleus (nuclein) of cells are xanthine and guanine and other closely-related ureides. A few aromatic compounds also occur among the products of decomposition of proteins.

It is found convenient to divide the proteins into groups, according to certain differences in physical and chemical properties, but the line of demarcation is not sharp, and the classifications of different authors vary. Some proteins known as **native albumins,** such as egg- and serum-albumin, are soluble in water and are coagulated by heat ; others, **the globulins,** like

myosin of muscle and fibrinogen of blood, are insoluble in water, but soluble in saline and dilute acid and alkaline solutions. The **derived albumins** or **albuminates,** such as casein of milk and substances obtained by the action of acids or alkalis on native albumins and globulins, are soluble in acids and alkalis, but insoluble in water. The **proteoses** and **peptones** are extremely soluble in water, in acids, and in alkalis, and are not coagulated on heating. They are formed by the action of digestive enzymes, pepsin or trypsin, on the other proteids, and probably represent simpler molecular complexes, corresponding to the dextrins formed in the disintegration of starch.

Albuminoid substances.—In addition to the above compounds, there exists a group of amorphous nitrogenous substances resembling the proteins in many of their properties, but differing more widely among themselves than the proteins. They are included with the former in the general term **albuminoid** substances. Such substances are **mucin,** which gives the ropy consistency to many animal secretions; **gelatine** or **glutin,** which is obtained from connective-tissue, etc.; **keratin,** of which hair, nails, horn, etc., are chiefly composed; and **chitin,** which is present in the hard covering of invertebrates such as crabs and lobsters. Gelatine, or glue, is obtained from bones by dissolving out the inorganic matter (calcium phosphate, etc.) with dilute hydrochloric acid, and heating the elastic mass—which retains the shape of the bone—with water or with water under pressure. The substance is dissolved, and, on cooling, solidifies to a jelly. Skins heated with water also produce gelatine. Gelatine does not give all the reactions for proteins, but yields much the same products on hydrolysis with acids and alkalis, and by the action of the digestive ferments. It forms an insoluble compound with tannin, a property which is utilised in the production of leather (p. 300). When mixed with potassium dichromate and exposed to light, gelatine becomes insoluble in water. A number of photographic processes depend upon this property. It is also rendered insoluble by formaldehyde (p. 72).

The quantitative estimation of Nitrogen.—There are two principal methods for estimating nitrogen; one is known as Dumas' and the other as Kjeldahl's method.

Dumas' method.—The substance is burnt with copper oxide, as in an ordinary combustion, but in an atmosphere of carbon dioxide, and the free nitrogen is collected over caustic potash in a graduated cylinder. The combustion tube is filled, as shown in Fig. 56, with a roll of copper gauze, then with coarse oxide of copper, fine oxide of copper mixed with the weighed substance, and finally with a little more coarse oxide. The object of the copper roll is to reduce the oxides of nitrogen which might be formed and would then be absorbed by the potash solution. The tube is placed in a combustion furnace and attached to a *Schiff's azotometer*, shown in Fig. 57, for collecting the nitrogen. The tube is first filled with dry carbon dioxide so that all the air is

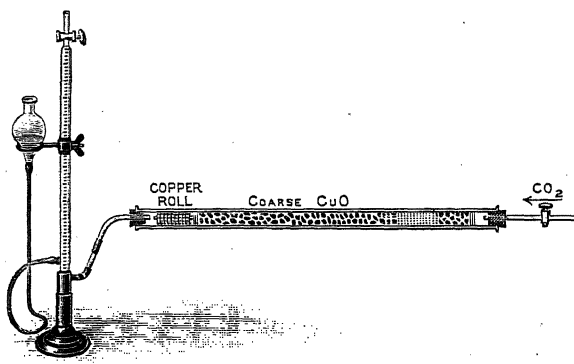


FIG. 57.—Dumas' apparatus for estimating nitrogen with Schiff's azotometer.

expelled and a slow current of the gas is maintained so as to drive out the nitrogen. During this period the potash is removed from the graduated tube by lowering the reservoir to which it is attached by rubber tubing and opening the tap. When the air has been expelled, the graduated tube is filled by raising the reservoir and the tap is then closed. The operation is conducted as in an ordinary combustion, the front of the combustion tube being first heated and then the substance, so that a slow stream of gas passes into the azotometer. When the evolution of nitrogen begins to slacken, the current of carbon dioxide is increased so as to drive out the last traces, and when there is no further increase in volume of nitrogen the process is stopped. The reservoir must be raised to the level of the liquid inside the volume, and the temperature and barometric pressure then be noted.

Example.—0·206 gram of substance gave 18·8 c.c. of moist nitrogen at 17° and 756 mm. (vapour pressure of potash solution at 17° = 14·5 mm.)

$$\frac{18{\cdot}8\times273\times(756-14{\cdot}5)\times0{\cdot}126}{(273+17)\times760\times0{\cdot}206}=10{\cdot}56 \text{ per cent.}$$

Kjeldahl's method.—The organic compound is heated strongly with sulphuric acid, which oxidises the organic matter and converts the nitrogen into ammonium sulphate. The ammonia is then estimated volumetrically by distilling with caustic soda and collecting the gas in standard acid. About 0·5 gram of substance is accurately weighed and introduced into a round Jena flask (500 c.c.), together with 15 c.c. of pure concentrated sulphuric acid and about 10 grams of anhydrous potassium sulphate. The object of the latter is to promote oxidation by raising the boiling-point of the liquid. The flask is clamped over wire-gauze and the contents boiled briskly until the liquid, which first darkens in colour, becomes clear and colourless, or faintly yellow. When the decomposition is complete (½—1 hour), the flask is left to cool and the contents then diluted with 2—3 volumes of water. The flask is now attached to the distilling apparatus shown in Fig. 58. It is furnished with a rubber cork, through which a bulb adapter is inserted (to retain any alkali which may spirt upwards), the latter being connected with a condenser. The end of the condenser just dips below the surface of 25 c.c. of a half-normal solution of hydrochloric or sulphuric acid, contained in a flask or beaker. A fewer pieces of porous earthenware or granulated zinc are introduced into the flask to prevent bumping. About 30 grams of caustic soda in 60 c.c. of water are poured in carefully down the side of the flask and the cork quickly inserted. The liquid is then boiled briskly until no more ammonia is evolved (½—¾ hour). This should be ascertained by testing a drop of the distillate with red litmus paper. If the operation is complete, the liquid is titrated with half-normal sodium

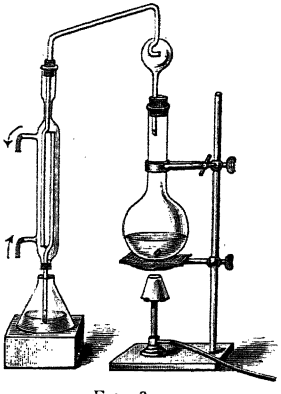


FIG. 58.

carbonate or caustic soda solution, using methyl orange as indicator.

Example.—0·5151 gram of substance required 17·3 c.c. *N*/2 sodium carbonate:

$$25-17{\cdot}3=7{\cdot}7. \quad \frac{7{\cdot}7\times 0{\cdot}007\times 100}{0{\cdot}5151} = 10{\cdot}46 \text{ per cent.}$$

QUESTIONS ON CHAPTER XIX

1. What is meant by the term amino-acid? What are its properties? In what respect does it differ from an amide?

2. Describe the preparation of glycine. How can it be converted into glycollic acid?

3. What is hippuric acid? How is its constitution determined? Name other derivatives of glycine obtained from natural sources and give their formulæ.

4. Give the reactions for the proteins. Describe some of their decomposition products.

5. Name some of the chief groups of proteins and their characteristic properties.

6. What is meant by the term albuminoid substance?

7. How is gelatine obtained? Name some of its properties. How could it be distinguished from egg-albumin?

8. Describe any application of proteins in the arts or manufactures.

9. Estimate the percentage of nitrogen in an organic compound from the following data: 0·2002 gram gave 17·5 c.c. of moist nitrogen at 14° and 759 mm.

10. Calculate the percentage of nitrogen estimated by Kjeldahl's method from the following data: 0·5 gram of the substance was decomposed and distilled with caustic soda and the ammonia collected in 50 c.c. of normal sulphuric acid. The acid then required 33·6 c.c. of normal caustic soda solution for neutralisation.

PART III

AROMATIC COMPOUNDS

CHAPTER XX

THE AROMATIC HYDROCARBONS

The meaning of "Aromatic."—The name aromatic was originally applied to a small group of compounds which could not be classed among existing families of the better-known aliphatic series. The members of this group, which included the balsams and resins, and products derived from them, essential oils, like bitter almond oil, turpentine oil, oil of wintergreen, of cloves, and of lemon, etc., possessed in common an aromatic smell.

On closer study, many were found to possess properties not very dissimilar from those of aliphatic compounds, and to be similarly related among themselves. For example, toluene is a liquid hydrocarbon originally obtained from tolu balsam; oil of bitter almonds is an aldehyde; and benzoic acid is an acid, derived from gum-benzoin. They can be converted into one another, and stand in the relation of paraffin, aldehyde, and acid.

C_7H_8	C_7H_6O	$C_7H_6O_2$.
Toluene.	Oil of bitter almonds.	Benzoic acid.
C_2H_6	C_2H_4O	$C_2H_4O_2$.
Ethane.	Acetaldehyde.	Acetic acid.

But notwithstanding this parallelism which appeared among members of the two series, a sharp line divided the aliphatic

from the aromatic compounds. Indeed, some years elapsed before any direct synthesis of a member of the one group from that of the other served as a connecting link between them.

The aromatic compounds contain a higher percentage of carbon; hexane, C_6H_{14}, contains 83·7 per cent., whereas benzene, C_6H_6, which is the simplest hydrocarbon of the aromatic series, contains 93·6 per cent. of carbon.

EXPT. 118.—Burn some hexane and benzene side by side on two inverted porcelain lids and note the much larger separation of soot in the flame of benzene.

The more complex members of the aromatic series may be broken up by the action of various reagents into simpler substances, such as benzene, (C_6H_6), phenol, (C_6H_6O), picric acid, ($C_6H_3O_7N_3$), etc.; but any attempt to pass beyond this point, and to form substances with five or fewer carbon atoms, generally results in the complete disintegration of the molecule. Toluene may be oxidised to benzoic acid (p. 256); and benzoic acid, when distilled with soda-lime, loses carbon dioxide and yields benzene:

$$\underset{\text{Benzoic acid.}}{C_7H_6O_2} = \underset{\text{Benzene.}}{C_6H_6} + CO_2.$$

But if benzene is decomposed by oxidation, it forms carbon dioxide and water, and no intermediate products are obtained.

Kekulé's Theory.—It was upon the existence of this residual nucleus of six carbon atoms, which appeared in the ultimate products of decomposition of aromatic substances, that Kekulé founded his celebrated benzene theory. The aliphatic compounds are **open-chain** compounds; benzene, which is the fundamental hydrocarbon of the aromatic series, as methane is of the aliphatic series, possesses a **closed-chain** or **ring** of carbon atoms.

Let us suppose the six carbon atoms of benzene to be arranged in a horizontal row, and a hydrogen atom attached to a bond of each of the carbon atoms:

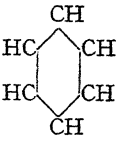
—CH.CH.CH.CH.CH.CH—

The number of carbon- and hydrogen-atoms corresponds to

the formula of benzene. Let us now modify the above arrangement by attaching the two end carbon atoms:

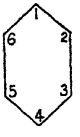
CH.CH.CH.CH.CH.CH.

A closed chain or ring results, which is usually represented in the form of a regular hexagon[1]:



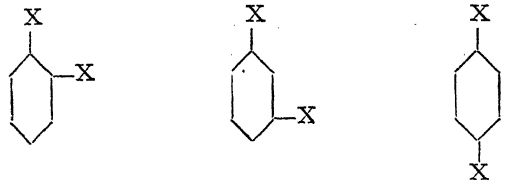
The existence of such a closed system of atoms presents nothing unusual, when we consider the structure of the anhydrides of dibasic acids (p. 182) and of the ureides (p. 227). This arrangement furnishes an explanation of many well-known properties of benzene. It explains its unusual stability towards reagents. It accounts for the existence of only one mono-derivative of benzene (that is, a derivative obtained by replacing one of the hydrogen atoms by another element or group); for the hydrogen atoms being symmetrically distributed, the six positions are identical. It explains, moreover, the occurrence of three isomeric di-derivatives. Isomeric di-derivatives of benzene are very common, but the maximum number is always three. There are three dichlorobenzenes, $C_6H_4Cl_2$, three dibromobenzenes, $C_6H_4Br_2$, three dinitrobenzenes, $C_6H_4(NO_2)_2$, etc.

Suppose we number the carbon atoms of the benzene ring from 1 up to 6, and represent the two new elements or groups by X. The positions which they can take are, 1, 2; 1, 3; 1, 4; 1, 5, and 1, 6.



[1] The hexagon is elongated in the figures, partly to economise space when a number of them are drawn side by side, partly to assist the memory in retaining the relative positions of substituted hydrogen atoms by giving the figure somewhat different dimensions in horizontal and vertical directions.

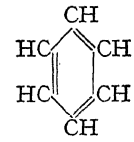
It is clear, however, that positions 1, 2 and 1, 3 are identical with 1, 6 and 1, 5. Three positions, therefore, remain, which will be those of the three isomers referred to above. These positions are known as **ortho-**, **meta-**, and **para-positions.**[1]



Ortho- Meta- Para-

Positions of the groups in the three isomeric di-derivatives of Benzene.

It will be seen from the above formula for benzene that only three bonds of each carbon atom are appropriated—two for union with the adjoining carbon atoms and one for attaching the hydrogen atom. What is the function of the fourth carbon bond? In Kekulé's original formula the carbon atoms were linked alternately by double and single bonds:



Kekulé's formula for Benzene.

This formula represents an unsaturated hydrocarbon of the olefine family (p. 127). Benzene, in fact, possesses the properties of an olefine, inasmuch as it forms the following additive compounds with hydrogen, chlorine, bromine, and hypochlorous acid:

C_6H_{12}	$C_6H_6Cl_6$	$C_6H_6Br_6$	$C_6H_6(HClO)_3$
Hexahydro-benzene.	Benzene hexachloride.	Benzene hexabromide.	Benzene trichlorhydrin.

The fact that the maximum number of monovalent atoms which are required to saturate benzene is 6 and no more, is

[1] The names *ortho*, *meta*, and *para* will be occasionally indicated by the initial letters *o-*, *m-*, *p-* before the name of the substance. The numbers will also be used to denote the relative positions of atoms, or groups, in the ring.

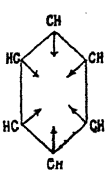
taken as strong evidence of the existence of 3 double linkages, and consequently of a closed chain.

On the other hand, Kekulé's formula for benzene fails to account for some of the characteristic properties of the olefines, which possess double linkages. Benzene and its derivatives form no additive compounds with the halogen acids, or strong sulphuric acid; nor are they, as a rule, oxidised in the cold by a solution of potassium permanganate, which rapidly attacks the olefines and their derivatives. Furthermore, the positions 1, 2 and 1, 6 are not strictly identical, for a double link is interposed between one pair of carbon atoms and a single link between the other pair:



Consequently, 4 and not 3 di-derivatives should exist, and no example of the kind is known.

Kekulé's formula has therefore met with some opposition. The fate of the fourth carbon bond has been a long-debated problem. In order to sever the connection of benzene with the olefines, the fourth carbon bond has been described as a **centric, potential,** or **residual** valency, which signifies a modified bond of a somewhat ill-defined character. What is known as the **centric formula** for benzene was suggested by Armstrong and supported by the experimental evidence of Baeyer, but cannot



Armstrong and Baeyer's centric formula for Benzene.

be discussed here. The fourth or centric bond is represented as an arrow directed towards the centre of the hexagon.

For practical purposes the fourth carbon bond may be omitted from the formula, and until something more definite transpires concerning it, the simple hexagon formula will suffice. Before entering upon a more elaborate discussion of the evidence upon which the hexagon formula rests—that is to say, the symmetrical distribution of carbon and hydrogen atoms in the molecule—it will be necessary to study in greater detail the properties of the aromatic hydrocarbons.

The Aromatic Hydrocarbons

Distillation of Coal-Tar.—The principal source of benzene and its homologues is coal-tar. Coal-tar is produced in the

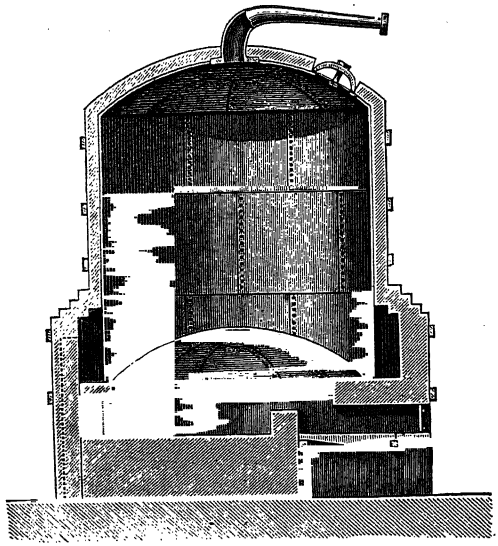


Fig. 58A.—Tar still.

manufacture of coal-gas by the destructive distillation of coal in fire-clay retorts. The gases from the retorts pass through a series of upright pipes or air-condensers, which rise from a long trough in which the tar collects, whence it is drawn into a tank,

or tar-well. Tar is also produced in considerable quantities in the manufacture of coke in coke-ovens. The quantity of tar varies with the character of the coal employed, 10 to 20 gallons being usually obtained from each ton of coal. When the tar is submitted to fractional distillation, it yields a variety of volatile products of different boiling-points, which form the material from which the majority of aromatic compounds are prepared. Coal-tar is distilled in large wrought-iron stills, holding from 20 to 30 tons. Fig. 58A represents a section of a tar still. It is surrounded by brick-work, and heated by a fire below. The still-head is connected with a condensing worm (not shown in the drawing), from which the condensed products are conducted into different receivers.

The distillate is usually divided into the following fractions, although different works vary slightly in their mode of working:

Distillate.	Distilling temperature.	Constituents of the fraction.
Light oil, or Crude Naphtha	to 170°	Benzene and homologues.
Middle, or Carbolic oil	to 230°	Carbolic acid and Naphthalene.
Heavy, or Creosote oil	to 270°	Constituents not usually separated.
Anthracene oil	above 270°	Anthracene.
Pitch	residue in the still	—

The terms "light," "middle," and "heavy" oil denote the specific gravity of the distillate. During the distillation a sample is run into water. If it floats it is known as **light oil**, if it sinks it is called **heavy oil**. A certain quantity is collected after the light oil ceases to distil, and this is the **middle oil**. The separation of the fractions is often determined by the boiling-point of the distillate, which is indicated by a thermometer fixed in the still. Each of the fractions is worked up and separated into its constituents, except the creosote oil, which is employed as it comes from the still for preserving timber. One hundred

parts of tar yield the following approximate quantities of commercial products:

Benzene and homologues	1·40
Carbolic acid	0·20
Naphthalene	4·00
Creosote oil	24·00
Anthracene	0·20
Pitch	55·00
Water	15·00
	99·80

The separation of the constituents from the different fractions will be dealt with later, when the substances themselves are described. We shall confine our attention at present to the first fraction, or light oil. This fraction is usually redistilled, and the portion boiling between 80° and 150° is worked up for benzene and its homologues. It contains basic substances—aniline, (p. 131), pyridine (p. 312), etc.—which are dissolved out by agitation with strong sulphuric acid. The acid is then withdrawn, and the oil treated with caustic soda solution, which removes any residual sulphuric acid as well as carbolic acid. This is followed by agitation with water, after which the purified oil is fractionated. A special form of still is used, which is heated by steam, and is furnished with a long fractionating column. The fraction, which is first collected, is known as benzene, b.-p. 80°–81°, then toluene, b.-p. 110°, and xylene, b.-p. 137°–140°.[1] The higher-boiling fraction, known as **solvent naphtha,** is used for dissolving rubber in the preparation of waterproof fabrics, or as **burning naphtha,** which is employed for illuminating purposes.

Benzene, C_6H_6, was discovered by Faraday (1825). Before the introduction of coal-gas, a little illuminating gas was manufactured from oil, and delivered to consumers compressed into cylinders. By cooling the gas from these cylinders in a freezing mixture, a liquid was obtained from which Faraday separated benzene by distillation. Benzene was afterwards obtained by distilling calcium benzoate with slaked lime. The benzoate decomposes into benzene and calcium carbonate, a

[1] The commercial names are benzol, toluol, and xylol.

process which recalls the formation of marsh-gas from sodium acetate (p. 60):

$$\underset{\text{Calcium benzoate.}}{(C_6H_5CO_2)_2Ca} + Ca(OH)_2 = 2\underset{\text{Benzene.}}{C_6H_6} + 2CaCO_3.$$

EXPT. 119.—Grind together 30 grams of calcium benzoate with twice its weight of soda-lime, and distil the mixture from a retort, which must be attached to a condenser and receiver. Water and a light brown oil distil, smelling strongly of benzene. The benzene can be separated from the water by a small tap-funnel. It is then dried over calcium chloride, and redistilled.

Benzene has been synthesised by Berthelot from acetylene (p. 135), by heating the gas in a closed vessel at a moderately low temperature. The acetylene polymerises, and forms benzene:

$$\underset{\text{Acetylene.}}{3C_2H_2} = \underset{\text{Benzene.}}{C_6H_6}.$$

Benzene is now exclusively obtained from coal-tar in the manner already described.

The commercial product always contains a small quantity of an organic sulphur compound, known as **thiophene**, C_4H_4S, which is a colourless liquid and has nearly the same boiling-point as benzene.

EXPT. 120.—The distillation of coal on a small scale may be shown by means of the apparatus (Fig. 26, p. 55). Small pieces of coal are placed in the tube attached to a dry wash-bottle and delivery tube connected with a gas jar standing over water. On heating the coal, gas is given off, water and tar distil and collect in the wash-bottle. The water contains ammonia and has a strongly alkaline reaction. The tar contains the benzene hydrocarbons, etc.

Properties of Benzene.—Benzene is a colourless liquid with a peculiar smell. It boils at 80°·5, solidifies at 5°·4, and has a specific gravity of 0·874 at 20°. It is very inflammable, and burns with a luminous and smoky flame. It is insoluble in water, and, having a lower specific gravity, floats on the surface. It is sometimes used like ether for separating organic liquids when mixed with water, also for extracting fats, etc., and for dry cleaning.

The chemical properties of benzene may be taken as typical of the family of aromatic hydrocarbons. Benzene resists the

action of all the ordinary oxidising and reducing agents. Hydrogen in presence of colloidal platinum at the ordinary temperature, or finely divided nickel at about 160°, converts it into the **hexahydride**, C_6H_{12}. When benzene is exposed to the action of chlorine or bromine in sunlight, crystals of **benzene hexachloride**, $C_6H_6Cl_6$, or **hexabromide**, $C_6H_6Br_6$, slowly deposit. Both substances are very unstable, and emit a smell of chlorine or bromine.

If chlorine or bromine acts upon benzene in presence of a "carrier," substitution occurs, and a series of chlorinated or brominated products is formed, containing from one up to six atoms of the halogen in place of hydrogen:

$$C_6H_6+Cl_2=\underset{\text{Monochloro-benzene.}}{C_6H_5Cl}+HCl, \qquad C_6H_5Cl+Cl_2=\underset{\text{Dichloro-benzene.}}{C_6H_4Cl_2}+HCl,$$

and so forth.

EXPT. 121.—Pour a few c.c. of benzene into three test-tubes and add some drops of bromine to each. Into one of the test-tubes drop a small piece of aluminium-mercury couple (see Expt. 122); to a second add some iron filings. Notice the difference in the action as indicated by the evolution of hydrobromic acid from the three test-tubes.

Iodine has no direct action on benzene or the other hydrocarbons and in this respect the latter resemble the paraffins.

The preparation of bromobenzene is conducted on a larger scale as follows:

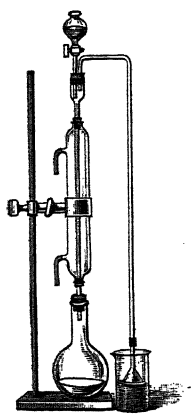


FIG. 59.

EXPT. 122.—**Preparation of Bromobenzene.**—The apparatus is shown in Fig. 59. Fifty grams of benzene are placed in the flask and 120 grams of bromine (40 c.c.) in the tap-funnel. About 0·5 gram of aluminium foil is covered with a solution of mercuric chloride until the surface is coated with mercury. After being washed two or three times with water, alcohol, and then with benzene it is dropped at once into the flask. The bromine is now allowed to drop in slowly. The couple becomes coated with a brown film and a vigorous action takes place with evolution of hydrogen bromide which collects in the beaker containing

water. When all the bromine has been introduced and the *red* colour has disappeared from the flask (a dark colour still remains), water is added; the mixture is well shaken and then a little caustic soda solution until the liquid is alkaline and it is well shaken again. The mixture, which separates into two layers, is poured into a tap-funnel, the lower layer (bromobenzene) drawn off, shaken a second time with a little more caustic soda solution and separated. It is then dehydrated over calcium chloride, filtered and distilled. The distillate is collected at 150°–160°. The yield is 60 grams. The boiling-point is 155°.

Dilute nitric acid has no action on benzene, but strong nitric acid rapidly attacks it, and forms nitro-derivatives. The action is assisted by the presence of strong sulphuric acid, which absorbs the water formed in the process:

$$C_6H_6+HNO_3=\underset{\text{Nitrobenzene.}}{C_6H_5.NO_2}+H_2O.$$

$$C_6H_5NO_2+HNO_3=\underset{\text{Dinitrobenzene.}}{C_6H_4.(NO_2)_2}+H_2O.$$

EXPT. 123.—Mix together 20 c.c. of strong sulphuric acid and 15 c.c. of strong nitric acid in a graduated cylinder. Add half the volume of the mixed acid (17 c.c.) gradually to 5 c.c. of benzene, contained in a small flask; cool and shake well. Heat is evolved and nitrobenzene is formed. When the acid has been added, pour a little into water and notice that the liquid has a yellow colour, and, instead of floating on the surface like benzene, sinks in the water. Add the remainder of the acid at once to the remaining liquid in the flask, and heat for a quarter of an hour on the water-bath; then pour into a cylinder of water. The substance which now separates is no longer liquid; but a pale yellow, crystalline solid, which is the dinitro-compound.

These two operations are conducted on a larger scale as follows:

EXPT. 124.—**Preparation of Nitrobenzene.**—Fifty grams of benzene are placed in a flask, and in another 60 c.c. of concentrated nitric acid and 60 c.c. of concentrated sulphuric acid are mixed together and then cooled. The mixed acids are then slowly added from a tap-funnel to the benzene, and the contents of the flask are *well shaken* after each fresh addition. Nitrous fumes are evolved, and a considerable amount of heat developed. Care must, however, be taken that the temperature does not exceed 50°–60°, by immersing the flask, if necessary, in cold water. The nitrobenzene separates out as a

brown, oily layer on the surface of the acid liquid. When the acid has all been added, an operation which lasts about half an hour, the mixture is heated for about twenty minutes on the water-bath, and again well shaken. The contents of the flask, on cooling, are poured into a stoppered separating-funnel, the lower layer of acid is removed, and the nitrobenzene washed free from acid by shaking once with water (50 c.c.), then with dilute carbonate of soda solution, and again with water, the oil being each time withdrawn from the bottom of the vessel. The nitrobenzene, separated as carefully as possible from water, is allowed to stand over a few pieces of fused calcium chloride, and shaken occasionally until the liquid is clear. The yellow liquid is decanted, or filtered from the calcium chloride, and distilled in a distilling-flask, with condenser tube only. At first a little benzene passes over; the temperature then rises, and the nitrobenzene distils at 204°–207°, and is separately collected. The brown residue consists of dinitrobenzene, the quantity depending upon whether the temperature during nitration has been allowed to rise too high. The yield is about 60 grams. Nitrobenzene is a pale yellow liquid with a smell of bitter almonds.

EXPT. 125.—**Preparation of *m*-Dinitrobenzene.**—Mix together 24 c.c. of fuming nitric acid sp. gr. 1·5 and 20 c.c. of concentrated sulphuric acid and add 30 grams of nitrobenzene in portions of 5–10 c.c. at a time. Heat is evolved, and the mass becomes somewhat deeper in colour. When the nitrobenzene has been added, the flask is heated for a short time on the water-bath. A few drops are then poured into a test-tube of water. The dinitrobenzene should, if the reaction is complete, separate as a hard pale yellow cake. If it is semi-solid, the heating must be continued. The contents of the flask are then poured, whilst warm, into a large quantity of water. The dinitrobenzene, which separates, is filtered at the pump and well washed with water. It is then dried. The yield is nearly theoretical. A few grams should be recrystallised from spirit (m.p. 90°). The remainder may be used for a subsequent preparation (p. 264).

Strong sulphuric acid, on warming, gradually dissolves benzene, and forms benzene sulphonic acid. Fuming sulphuric acid converts the latter into benzene disulphonic acid:

$$C_6H_6+H_2SO_4=\underset{\text{Benzene sulphonic acid.}}{C_6H_5.SO_3H}+H_2O.$$

$$C_6H_5.SO_3H+H_2SO_4=\underset{\text{Benzene disulphonic acid.}}{C_6H_4(SO_3H)_2}+H_2O.$$

EXPT. 126.—Mix together in a boiling-tube about 3 c.c. of benzene and 10 c.c. of strong sulphuric acid, and heat gently with constant shaking. The benzene, which at first floats on the acid, gradually dissolves with rise of temperature. When a little of the mixture is poured into water, a clear solution of benzenesulphonic acid is obtained.

On a larger scale the process is conducted as follows:

EXPT. 127.—**Preparation of Sodium benzene sulphonate.**—Mix together in a round flask, fitted to a reflex condenser and placed on a sand-bath, 60 c.c. of benzene and 60 c.c. of concentrated sulphuric acid. The mixture is kept at a gentle boil *with frequent shaking* until the top layer of benzene has been nearly absorbed by the sulphuric acid (six to eight hours). On cooling, the dark-coloured liquid is poured into cold water (1 litre) contained in a large basin, boiled up and neutralised with powdered chalk or thick milk of lime. The mass is filtered hot through a porcelain funnel or cloth from the precipitate of calcium sulphate, washed with hot water and somewhat concentrated. The solution, which contains the calcium salt of benzene sulphonic acid, is treated with just sufficient sodium carbonate solution to precipitate the calcium as carbonate and convert the sulphonic acid into the sodium salt. This is ascertained by filtering small samples and testing the filtrate with sodium carbonate. The liquid is again filtered through cloth or through a porcelain funnel and concentrated, first over a ring burner and finally on the water-bath, until a sample crystallises on cooling. The sodium salt is drained at the pump and dried on porous plate. The yield is about 80 grams.

The action of strong nitric and sulphuric acids on benzene, in producing nitro-derivatives in the one case, and sulphonic acids in the other, is a characteristic property of aromatic compounds. The homologues of benzene, as well as the majority of benzene derivatives, combine with these two acids in the manner described. In this respect the aromatic compounds offer a marked contrast to the paraffins, and the other aliphatic hydrocarbons.

Toluene.—**Methyl benzene, Phenyl methane,** $C_6H_5.CH_3$.—Toluene received its name from a resin, known as tolu balsam, from which it is obtained by distillation. It is now separated by fractional distillation from coal-tar naphtha by the method

already described (p. 246). Toluene closely resembles benzene in properties. It is a colourless liquid with an odour resembling benzene. It boils at 110°, solidifies at −98° and has a sp. gr. 0·869 at 16°. The relation of toluene to benzene has been determined by decomposition and synthesis. It has already been stated that toluene may be oxidised to benzoic acid, and the latter converted by distillation with lime into benzene. The synthetic processes used in its preparation are known as the methods of Fittig, and of Friedel and Crafts.

Fittig's method recalls that employed by Wurtz in the synthesis of the paraffins (p. 77). It consists in mixing together bromobenzene and methyl iodide, diluted with dry ether, and adding sodium in thin slices. The action commences spontaneously, and, when it ceases, the liquid is decanted from the sodium salts, and the toluene separated by fractional distillation:

$$\underset{\text{Bromo-benzene.}}{C_6H_5Br} + \underset{\text{Methyl iodide.}}{CH_3I} + Na_2 = \underset{\text{Toluene.}}{C_6H_5.CH_3} + NaBr + NaI.$$

The Friedel-Crafts' Reaction.—In this reaction anhydrous aluminium chloride is added to benzene, and methyl chloride passed in, or methyl bromide added to the mixture. Hydrochloric, or hydrobromic acid is rapidly evolved, and toluene is formed. The product is poured into water, and the upper layer removed and fractionated. The action of the aluminium chloride is not fully understood, but is usually accounted for by the formation of an intermediate compound of benzene and aluminium chloride, which is decomposed by the alkyl halide. The reaction may be expressed as follows:

$$C_6H_6 + CH_3Cl[+AlCl_3] = C_6H_5.CH_3 + HCl.$$

By prolonging the action, additional methyl groups are introduced into benzene, and a series of di-, tri-, etc., methyl benzenes are formed.

Both Fittig's and Friedel-Crafts' reactions can be applied to the synthesis of a large number of aromatic hydrocarbons by substituting different alkyl halides for the methyl compounds. The Friedel-Crafts' method in particular has a very wide and varied application, for its action is not limited to the production

of hydrocarbons alone. Many other substances containing chlorine, such as the acid chlorides, unite in presence of aluminium chloride with benzene and its homologues, with the evolution of hydrogen chloride and the formation of new products. The acid chlorides yield ketones. Benzene, acetyl chloride, and aluminium chloride form phenyl methyl ketone:

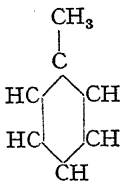
$$C_6H_6+CH_3.CO.Cl[+AlCl_3]=C_6H_5.CO.CH_3+HCl.$$

Phenyl methyl ketone.

It appears that only hydrocarbons of the aromatic series can enter into these reactions. Neither the paraffins nor olefines possess the property. The Friedel-Crafts' reaction is, therefore, recognised as a distinctive feature of the aromatic hydrocarbons.

EXPT. 128.—**The Friedel-Crafts' reaction.**—Pour a few c.c. of benzene into a test-tube; add about a gram of anhydrous aluminium chloride and then a few drops of ethyl bromide. Hydrobromic acid is at once evolved. If the product is poured into water, the upper layer contains ethyl benzene, which, on a larger scale, would be separated by fractional distillation. Repeat the experiment, using acetyl chloride in place of ethyl bromide, and pour the product into caustic soda solution. The upper layer contains methyl phenyl ketone, which possesses a characteristic sweet smell.

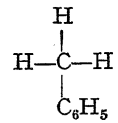
Structure of Toluene.—The synthesis of toluene from benzene clearly explains its structure. Toluene is the methyl derivative of benzene, the graphic formula of which is represented as follows:



Structural formula for Toluene.

Toluene is also known as phenyl methane. The term **phenyl** denotes the monovalent radical, C_6H_5', of benzene, just as ethyl, C_2H_5', stands for the radical of ethane. The name is derived from the Greek *φαίνω*, to illuminate, from the connection of

benzene with the coal-gas manufacture.[1] It is equally correct to represent toluene as methane in which a phenyl group replaces an atom of hydrogen:



Toluene, or Phenyl methane.

Nucleus and Side-chain.—It is found convenient to draw a distinction between the purely aromatic part, or ring, and the aliphatic part, or alkyl group, in a compound like toluene. The aromatic, or benzenoid part is known as the **nucleus,** whilst the aliphatic, or paraffinoid part is denoted by the term **side-chain.** We say that toluene contains a nucleus and a side-chain.

A peculiarity of the side-chain is the effect produced upon it by oxidising agents. This has already been mentioned (p. 242). The side-chain is converted into a carboxyl group, the nucleus remaining intact. Toluene forms benzoic acid. The same result is produced if the side-chain is an ethyl, propyl, or other alkyl group, containing several carbon atoms; it breaks down on oxidation in the same manner as toluene, and forms the same product, viz. benzoic acid. The value of this property in studying the structure of aromatic hydrocarbons and their derivatives is very considerable, and is well illustrated in the case of the xylenes (p. 258).

Action of Chlorine on Toluene.—Toluene, like benzene, undergoes substitution by chlorine and bromine. Substitution is not, however, limited to the nucleus. Hydrogen may be replaced in the side-chain. Substitution takes place in the side-chain if chlorine is passed into boiling toluene, and the following three products are successively produced:

$C_6H_5.CH_2Cl$	$C_6H_5.CHCl_2$	$C_6H_5.CCl_3$.
Benzyl chloride.	Benzylidene, or Benzal chloride.	Benzenyl chloride, or Benzotrichloride.

The first contains the monovalent radical benzyl, $C_6H_5.CH_2'$, corresponding to ethyl; the second, benzylidene, $C_6H_5.CH''$,

[1] The generic term for the aromatic radicals is *aryl*, which corresponds to alkyl of the aliphatic series.

corresponding to ethylidene; the third, the radical benzenyl, $C_6H_5.C'''$.

EXPT. 129.—**Preparation of Benzyl chloride.**—One hundred grams of toluene are poured into a retort together with one gram of phosphorus trichloride and roughly weighed. The retort is placed on wire gauze and attached to a reflux condenser which is furnished at the top with a delivery tube to absorb the hydrogen chloride as shown in Fig. 59, p. 250, or placed in a fume cupboard. A rapid stream of dry chlorine is passed through the boiling liquid until it has gained about 37 grams in weight. The liquid turns yellow, and hydrochloric acid fumes are evolved. When the reaction is complete the contents of the

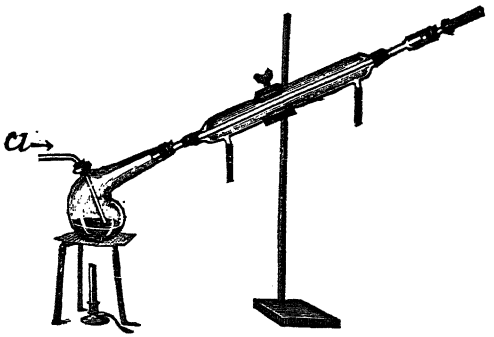


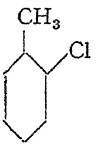
FIG. 60.

retort are distilled. At first unchanged toluene distils; the fraction boiling at 165°–185° contains nearly the whole of the benzyl chloride, and forms the greater part of the product. The liquid, which passes over above 185°, is a mixture of higher chlorinated compounds, and consists chiefly of benzal chloride, $C_6H_5CHCl_2$, and benzotrichloride, $C_6H_5CCl_3$. The portion containing the benzyl chloride is repeatedly fractionated until a liquid is obtained, boiling at 176–180°, which is nearly pure benzyl chloride. The yield is 80–90 grams.

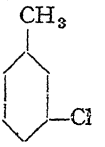
$$C_6H_5CH_3+Cl_2=C_6H_5CH_2Cl+HCl.$$

If, on the other hand, chlorine is passed into cold toluene to which a little antimony chloride, aluminium-mercury couple, iodine, or other carrier is added, substitution is confined to the nucleus, and mono-, di-, tri-, etc., chlorotoluenes are formed.

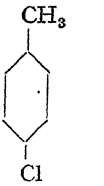
There are three monochlorotoluenes, the ortho-, meta-, and para-compounds, which are isomeric with benzyl chloride, so that there are in all four compounds of the formula C_7H_7Cl. In the following formulæ the carbon and hydrogen atoms of the nucleus are omitted:



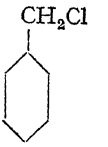
Ortho-chlorotoluene.



Meta-chlorotoluene.



Para-chlorotoluene.



Benzyl chloride.

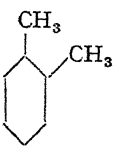
There is a marked difference in the properties of the halogen derivatives of the aromatic hydrocarbons containing the halogen in the side-chain and in the nucleus.

The halogen in the nucleus is very difficult to remove, whereas that in the side-chain behaves like the halogen in the aliphatic compounds. Benzyl chloride undergoes reactions quite similar to those of ethyl bromide:

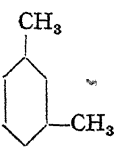
$$C_6H_5CH_2Cl + KOH = C_6H_5CH_2OH + KCl.$$
$$C_6H_5CH_2Cl + 2NH_3 = C_6H_5CH_2NH_2 + NH_4Cl.$$
$$C_6H_5CH_2Cl + KCN = C_6H_5CH_2CN + KCl.$$

EXPT. 130.—Shake a little bromobenzene, benzyl chloride and ethyl bromide in separate test-tubes with an alcoholic solution of silver nitrate and notice the rate at which the silver halide is formed in each case.

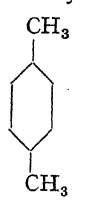
Hydrocarbons of the Formula C_8H_{10}.—Theory requires four isomeric hydrocarbons of the formula C_8H_{10}, viz. ortho-, meta-, and para-dimethylbenzene and an ethyl benzene:



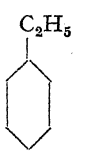
Ortho-dimethylbenzene.



Meta-dimethylbenzene.



Para-dimethylbenzene.

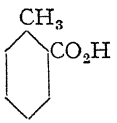


Ethyl-benzene.

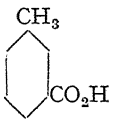
The three dimethylbenzenes, which are termed **xylenes**, are all present in coal-tar, the meta-compound largely predominating. They cannot be separated by fractional distillation, as the boiling-points lie too close together, and commercial xylene is therefore a mixture of the three isomers.

	Boiling-point.
Ortho-xylene	142°
Meta-xylene	137°
Para-xylene	137°

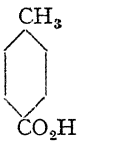
Oxidation of the Xylenes, etc.—The behaviour of the four compounds on oxidation is instructive, as illustrating the manner in which the constitution of an aromatic hydrocarbon may be studied. When the hydrocarbon is oxidised, the side-chains are converted into carboxyl groups as already explained (p. 256). Ethyl benzene gives benzoic acid, and consequently contains one side-chain. The xylenes, on the other hand, yield dibasic acids containing two carboxyl groups. The process occurs in two stages; the two methyl groups being converted successively into carboxyl groups. The first products are known as toluic acids:



Ortho-toluic acid.

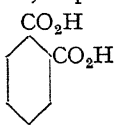


Meta-toluic acid.

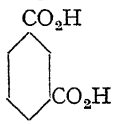


Para-toluic acid.

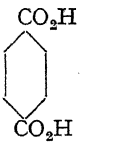
Each of these gives rise to a dibasic acid, known respectively as phthalic, isophthalic, and terephthalic acid:



Phthalic acid.



Isophthalic acid.



Terephthalic acid.

Other aromatic hydrocarbons, known as pseudocumene (1 : 2 : 4-trimethylbenzene), mesitylene (1 : 3 : 5-trimethylbenzene), and cymene (*p*-isopropyl methyl benzene), occur in coal-tar, but require no special mention, as their properties are similar to the hydrocarbons already described.

The Terpenes, Caoutchouc, and Gutta-percha are hydrocarbons possessing the general formula $(C_5H_8)_n$ which are closely related to the aromatic hydrocarbons, more especially to cymene. The terpenes have the general formula $C_{10}H_{16}$, and are common constituents of the sweet-smelling, volatile oils extracted from plants (essential oils). **Pinene** is the chief constituent of oil of turpentine, **limonene** of oil of lemons. Turpentine oil (which is obtained by the distillation of rosin) is soluble in most organic solvents and is used as a vehicle for pigments and in the manufacture of varnishes, etc. It oxidises in the air, forming a resinous substance, and rapidly absorbs ozone. **Caoutchouc** (rubber) and **guttapercha** are extracted as viscid emulsions (*latex*) by making incisions into the bark of certain trees (guttapercha from trees of the order of *Sapotaceæ* found in the Malay peninsula and rubber from *Hevea brasiliensis, manihot,* etc., cultivated in Brazil, Ceylon, and other tropical countries).

The emulsion coagulates on standing or more rapidly on heating, and is the source of the well-known materials found in trade. The natural rubber is usually treated with sulphur or sulphur compounds, with which it combines and then retains its elastic properties for a longer period. The product is termed vulcanised rubber. These two substances bear a similar relation to the terpenes as starch to glucose. They appear to be polymerides of the hydrocarbon isoprene, C_5H_8.

Camphor, borneol, and **menthol** are also natural products chemically related to the terpenes. Camphor, $C_{10}H_{16}O$, is a ketone and is extracted by steam distillation from the camphor tree (*Laurus camphora*) the chief source of which is the island of Formosa. Borneol, or borneo camphor, $C_{10}H_{17}(OH)$, is an alcohol and a reduction product of camphor, and is extracted from another tree (*Dryobalanops camphora*) growing in Borneo and Sumatra. Menthol, $C_{10}H_{19}(OH)$, is the chief constituent of peppermint oil and is the crystalline residue left after distilling the liquid terpenes.

QUESTIONS ON CHAPTER XX

1. Explain the origin and present meaning of the term *aromatic compounds*. Name some of the facts which suggested the view of a common nucleus in these compounds.

2. Explain why benzoic acid is said to be a benzene derivative. What relation does oil of bitter almonds bear to benzoic acid ?

3. Discuss the merits and demerits of Kekulé's formula for benzene, and those of any alternative formula.

4. Give an outline of the production of aromatic hydrocarbons from coal-tar.

5. By what physical and chemical properties are benzene and its homologues distinguished from all other hydrocarbons ?

6. Discuss the structural formula of toluene.

7. Give an account of the principal reactions of toluene which prove that it contains both a benzenoid and a paraffinoid residue. Describe precisely how you would conduct the operations and isolate the products.

8. Describe the Friedel-Crafts' and Fittig reactions for obtaining benzene hydrocarbons. Give at least one other example of the application of each of these important general methods of preparation.

9. How would you proceed to (1) identify an aromatic hydrocarbon ? (2) remove it from a mixture with petroleum ?

10. State how you would distinguish the isomeric hydrocarbons of the formula C_8H_{10}. How would you show that they are all derivatives of benzene ?

11. Give the formulæ of the isomeric xylenes, and state how one of them may be converted into phthalic acid.

12. Describe the action of (*a*) nitric acid and (*b*) sulphuric acid on benzene.

13. What is meant by the terms *nucleus* and *side-chain* ? How would you introduce chlorine into the one or other ?

14. Give a short account of the terpenes and substances related to them.

15. Name and give the constitutional formulæ of the isomeric bodies possessing the molecular formula C_7H_7Cl. Describe how any two of these are obtained and how they may be identified.

CHAPTER XXI

THE AMINO-COMPOUNDS AND THEIR DERIVATIVES

Amino-compound is the name usually given to those aromatic compounds in which the hydrogen of the nucleus is replaced by the amino-group. They correspond in structure to the aliphatic amines. Aminobenzene, or phenylamine, $C_6H_5.NH_2$, is the analogue of ethylamine, $C_2H_5.NH_2$. The term **amino-compound** rather than amine is preferred, inasmuch as the aromatic amino-compounds differ in many important respects from the aliphatic amines.

The amino-compounds cannot be obtained, as a rule, by the direct action of ammonia on the halogen substitution products of benzene and its homologues (p. 258), nor by any of the usual reactions which yield the aliphatic amines. The common method is one already referred to, viz. the reduction of the nitro-compounds in acid solution. The agents usually employed are the metals, iron, tin, and zinc, together with hydrochloric or acetic acid, stannous chloride dissolved in strong hydrochloric acid, or, in certain special cases, ammonium sulphide.

EXPT. 131.—**Preparation of Aniline from Nitrobenzene.**—Forty-five grams of granulated tin and 25 grams of nitrobenzene are placed in a round flask (1 litre). The contents are warmed for a few minutes on the water-bath. The flask is removed, and 90 c.c. of strong hydrochloric acid are gradually added in quantities of 5 to 10 c.c. at a time. The mixture sometimes boils up violently, in which case the flask should be immersed in cold water for a few minutes. In the course of half an hour all the acid should have been added. The flask is then heated on the water-bath for an hour to

complete the reduction. The reduction takes place according to the following equation:

$$2C_6H_5NO_2+3Sn+14HCl=2C_6H_5NH_2HCl+3SnCl_4+4H_2O.$$
Aniline hydrochloride.

If the liquid is allowed to cool at this stage, the double salt of aniline hydrochloride and stannic chloride, $(C_6H_5NH_2HCl)_2SnCl_4$, crystallises. Water is at once added, therefore, and a strong solution of caustic soda (70 grams in 100 c.c. of water). The aniline, which is liberated and floats on the surface as a dark-coloured oil, is separated by **distillation in steam.**

Distillation in Steam.—The apparatus used in this operation is shown in Fig. 61.

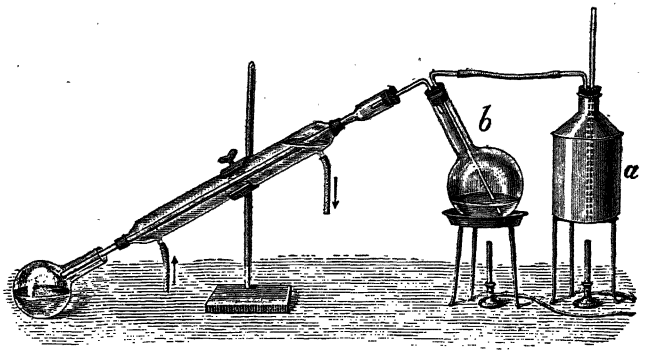


FIG. 61.—Distillation in steam.

The vessel *a*, which is an ordinary oil-can, is used to generate steam, and is partly filled with water. It is furnished with two tubes inserted through the cork. One tube, which is long and straight and open at both ends, serves as a safety-tube, by preventing liquid from being drawn from the flask *b* in case the flame under *a* is accidentally removed. The second tube is bent, and terminates just below the cork. It is attached by rubber tubing to the bent tube, which passes to the bottom of flask *b* containing the aniline. The flask *b* is connected with a condenser and receiver by a bent tube. The vessel *a* is heated directly by the flame, and the steam passes into *b*, which is heated on a sand-tray or wire-gauze, and is sloped to prevent the contents being splashed over into the condenser. The steam carries with it the vapour of aniline, which condenses and collects along with water in the receiver. The aniline in the receiver is separated by shaking with ether, which

dissolves the aniline. The ethereal layer is then removed, and dehydrated over solid caustic potash. The ether is distilled off on the water-bath, and the residual liquid is then distilled over the flame. Aniline boils at 181°–182°. The process of distillation in steam is one of great practical value, and is frequently employed where the substance is mixed with organic or inorganic impurities which do not volatilise. It may appear strange at first sight that aniline, which boils at 182°, can be distilled by passing in steam at a much lower temperature. The boiling-point of mixed liquids, which do not dissolve in one another, is determined by their combined vapour pressures. When this is equal to the external (atmospheric) pressure, both liquids distil. It follows, therefore, that aniline can be distilled much below its own boiling-point.

The conversion of a nitro- into an amino-group takes place in the presence of other groups, or, if there is more than one nitro-group in the nucleus, they all undergo reduction. Thus, dinitrobenzene gives diaminobenzene:

$$C_6H_4(NO_2)_2 + 6H_2 = C_6H_4(NH_2)_2 + 4H_2O.$$

Dinitrobenzene. Diaminobenzene.

It is possible to effect the reduction of the two nitro-groups in succession by using an alcoholic solution of ammonium sulphide. The dinitro-compound is dissolved in alcohol, strong ammonia is added, and hydrogen sulphide is passed through the solution until saturated. The reduction is effected by the hydrogen of the hydrogen sulphide and sulphur is deposited:

$$H_2S = H_2 + S.$$

The reaction in the case of dinitrobenzene is represented as follows:

$$C_6H_4(NO_2)_2 + 3NH_4HS = C_6H_4(NO_2)(NH_2) + 3NH_3 + 3S + 3H_2O.$$

Nitroaminobenzene, or Nitraniline.

EXPT. 132.—**Preparation of Meta-nitraniline.**—Dissolve 25 grams of dinitrobenzene prepared as described (Expt. 125, p. 252) in 95 c.c. of alcohol (purified spirit) and 13 c.c. of concentrated ammonia. Hydrogen sulphide washed through water is passed

into the dark red, pasty mass, which is occasionally shaken. The dinitrobenzene slowly dissolves, whilst, at the same time, flakes of crystallised sulphur are deposited. When the gas has been passing for an hour the flask is removed and heated on the water-bath for a few minutes. After cooling, the liquid is again saturated with hydrogen sulphide and then heated on the water-bath as before. When the gas has been passing in a steady stream for fully two hours the process is complete. Water is now added to the liquid until nothing further is precipitated. The mixture is filtered at the pump and washed with a little water. The solid residue is transferred to a flask and shaken up with successive small quantities of hot dilute hydrochloric acid and the liquid decanted through the original filter. The nitraniline dissolves, leaving the sulphur. When no more nitraniline is extracted (this may be ascertained by adding ammonia in excess to a portion of the acid solution, when no precipitate is formed), the acid solution is somewhat concentrated, cooled, and concentrated ammonia added. The *m*-nitraniline is precipitated, filtered when cold, and purified by recrystallisation from boiling water. The filtrate from the nitraniline may be concentrated on the water-bath and a further small quantity obtained. The yield is about 15 grams of yellow needles; m.-p. 114°.

Properties of the Amino-compounds.—The amino-compounds of the aromatic hydrocarbons are colourless liquids, or solids which are sparingly soluble in water, but dissolve in the common organic solvents. They may be distilled over the flame without decomposition, and are volatile in steam. They have a faint and not unpleasant smell, which, however, is not in the least ammoniacal. If other groups accompany the amino-group, the compound partakes of their physical characters.

The amino-compounds are bases. They form well-crystallised salts with acids and double salts with platinic chloride.

Aniline forms the following series of salts:

$C_6H_5NH_2.HCl$. Aniline hydrochloride. $C_6H_5NH_2.HNO_3$. Aniline nitrate. $(C_6H_5NH_2)_2H_2SO_4$. Aniline sulphate.

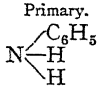
$(C_6H_5NH_2.HCl)_2PtCl_4$. Aniline platinochloride.

The hydrochlorides and nitrates of the bases are usually very soluble, the sulphates less soluble, in water. So far the compounds resemble the aliphatic amines. The bases, however,

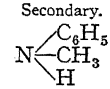
are not alkaline to litmus, nor are the salts neutral substances, but exhibit a strongly acid reaction with litmus. If a few crystals of pure aniline hydrochloride are dissolved in water, the solution will redden blue litmus. There are certain other organic colouring matters (methyl-violet, magenta, etc.) which are unchanged unless free acid is present, and are used for indicating neutrality when an acid is added to an aromatic base. This weakening of the basic properties of the amino-compounds is ascribed to the negative, or acid character of the benzene nucleus, which partially neutralises the basic properties of the amino-group. Diphenylamine, $NH(C_6H_5)_2$, which contains two phenyl groups, forms salts which are decomposed by water. Triphenylamine, $N(C_6H_5)_3$, does not combine with acids and forms no salts. We shall presently see that the negative character of the nucleus finds further expression in the enhanced acidic character of the hydroxy-compounds like phenol, $C_6H_5(OH)$, which forms salts with the caustic alkalis.

The amino-compounds form secondary and tertiary bases, like the amines, by replacement of the hydrogen atoms of the amino-group by radicals. The radical may be an alkyl group:

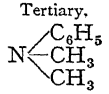
Primary. Secondary. Tertiary.



Aniline.

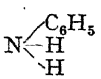


Methylaniline.

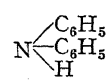


Dimethylaniline.

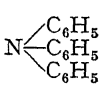
or, an aromatic radical like phenyl:



Aniline, or Phenylamine.

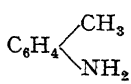


Diphenylamine.

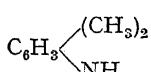


Triphenylamine.

Many of these substances are of great commercial importance. The homologues of aniline are called **toluidines, xylidines,** etc.



Toluidines.



Xylidines.

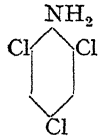
Reactions of Aniline.—The presence of aniline is readily detected by pouring a drop of the base into a solution of bleaching

powder or sodium hypochlorite. An intense violet coloration is produced, which slowly turns brown and fades.

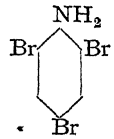
When aniline is oxidised with a cold solution of potassium dichromate and dilute sulphuric acid, it turns black, and the solution contains, among other products, **benzoquinone**, $C_6H_4O_2$.

Aniline undergoes the following reactions with the acids and halogens:

Chlorine and bromine act vigorously on aniline and form the 2 : 4 : 6-trichlor- and tribrom-aniline:



Trichloraniline.



Tribromaniline.

EXPT. 133.—**Preparation of Tribromaniline.**—Dissolve a few grams of aniline in dilute hydrochloric acid and add bromine water. A colourless precipitate of tribromaniline is produced, which may be filtered and crystallised from alcohol.

When aniline or aniline sulphate is heated with strong sulphuric acid aniline *p*-sulphonic acid or **sulphanilic acid** is formed:

$$C_6H_5NH_2 + H_2SO_4 = C_6H_4\begin{cases}NH_2\\SO_3H\end{cases} + H_2O.$$

EXPT. 134.—**Preparation of Sulphanilic acid.**—Mix together cautiously 25 grams of aniline and 45 c.c. of concentrated sulphuric acid in a round flask (250 c.c.) and heat to 180°–190° in an oil- or metal-bath for four to five hours until a sample dissolved in water remains clear on the addition of caustic soda in excess and no aniline separates. The product is poured into cold water, which precipitates the sulphanilic acid as a grey, crystalline mass. It is filtered, washed with a little cold water, recrystallised from hot water with the addition of a little animal charcoal, and dried in the air. It crystallises with 2 molecules of water of crystallisation, which it loses in the air. The yield is 25—30 grams.

Acetanilide, Phenylacetamide, Antifebrin, $C_6H_5NH.C_2H_3O$, is obtained by the action of acetyl chloride, or acetic anhydride,

on aniline, but is more economically prepared by boiling aniline with glacial acetic acid:

$$C_6H_5NH_2+C_2H_4O_2=C_6H_5NH.C_2H_3O+H_2O.$$
Acetanilide.

EXPT. 135.—**Preparation of Acetanilide.**—Mix together in a round flask (250 c.c.) fitted with a long straight upright tube (air condenser) 25 grams of aniline and 30 c.c. of glacial acetic acid and boil for seven hours. As the liquid solidifies on cooling, it is at once poured out, while hot, into a basin of cold water (500 c.c.). It is filtered and washed with cold water. Acetanilide crystallises best from hot water, in which, however, it is not very soluble. Place the moist acetanilide in a large basin, and add gradually about a litre of boiling water. If the substance does not dissolve completely on boiling, a small quantity of spirit will bring it into solution. Filter through a large fluted filter or porcelain funnel (p. 32) and set the solution aside to crystallise. If the product is dark coloured it is redissolved as before, and heated with a little animal charcoal (5–10 grams) for half an hour and then filtered. The yield is 30–35 grams. It crystallises in colourless plates; m.-p. 112°.

Introduce about 0·5 gram of the substance into a test-tube, and add 3 c.c. of concentrated hydrochloric acid. Boil for a minute. On diluting with water, a clear solution is obtained:

$$C_6H_5NHC_2H_3O+H_2O+HCl=C_6H_5NH_2.HCl+CH_3.CO_2H.$$

The acetanilide is hydrolysed, and forms aniline hydrochloride and acetic acid.

EXPT. 136.—**Preparation of Bromacetanilide.**—Dissolve 5 grams of acetanilide in 25 c.c. of glacial acetic acid and add gradually 2 c.c. (6 grams) of bromine and shake after each addition. When the bromine has been added, let the mixture stand ¼ hour and then pour into 200 c.c. of water and rinse out with water. Filter the crystalline precipitate at the pump and wash three or four times with water. Press it well down and let it drain. Dissolve the moist substance in spirit (about 60 c.c.) and pour into a beaker to crystallise. Filter the crystals, wash with a little dilute spirit, and dry on filter paper. The yield is 6–7 grams:

$$C_6H_5NH.C_2H_3O+Br_2=C_6H_4Br.NH.C_2H_3O+HBr.$$

Bromacetanilide crystallises in colourless needles; m.-p. 165°—166°. On hydrolysis with concentrated hydrochloric acid, *p*-bromaniline is formed (see above reaction for acetanilide).

Mono- and di-methylaniline are obtained by the action of methyl alcohol on aniline in presence of hydrochloric or sulphuric acid, the reaction taking place as follows:

1. $C_6H_5NH_2.HCl+CH_3OH=C_6H_5NH_2+CH_3Cl+H_2O$.

2. $C_6H_5NH_2+CH_3Cl=C_6H_5NHCH_3.HCl$.
Methylaniline hydrochloride.

3. $C_6H_5NHCH_3.HCl+CH_3OH=C_6H_5N(CH_3)_2.HCl+H_2O$.
Dimethylaniline hydrochloride.

Of the two, the dimethyl derivative is the more important technically. The ethyl derivatives are prepared in a similar fashion.

EXPT. 137.—**Preparation of Dimethylaniline.**—Twenty grams of aniline hydrochloride are prepared by gradually adding concentrated hydrochloric acid to aniline (20 grams in a beaker) until a drop brought on to a piece of filter paper, stained with methyl violet, turns it green. The liquid is quickly cooled and stirred so as to produce small crystals. It is then filtered, well pressed, and dried on a porous plate. The dry hydrochloride is brought into a thick-walled tube closed at one end, and the mixture of 15 grams of aniline and 22 grams of methyl alcohol added. The tube is then sealed in the ordinary way (Fig. 37, p. 105) and heated in the tube furnace gradually to 150° during two hours, and then to 180°–200° for six hours more. The contents of the tube divide into two layers, the lower consisting of the hydrochloride of the base and water, and the upper of the free bases. The whole of the contents are poured out into a large separating funnel, and caustic soda added in excess. The addition of a little ether causes the bases to separate out more readily. The top layer is removed, and the lower aqueous portion is shaken up twice with small quantities of ether. The ethereal solution is dehydrated over solid caustic potash, the liquid filtered, and the ether removed on the water-bath. The residue is now boiled with 25 grams of acetic anhydride (using an upright condenser) for an hour in the same flask, the side limb of which is stoppered. The contents are then distilled. Unchanged acetic anhydride passes over at 130°–150°; the temperature then rises, and the portion boiling at 190°–200° is

collected separately. When the higher temperature is reached, it is advisable to keep only the lower half of the condenser filled with water. The distillate has a bright amber colour. The yield is 20 grams. The residue in the flask consists of acetanilide and methylacetanilide and solidifies on cooling.

Distinction between Primary, Secondary, and Tertiary Amino-compounds.—The same reagents may be employed for distinguishing the three classes of amino-compounds as are used for the aliphatic amines, with similar, though not identical, results (p. 200).

If a solution of nitrous acid is added to a primary amino-compound and the liquid warmed, effervescence occurs, and the amino-group is replaced by hydroxyl. Aniline yields hydroxybenzene, or ordinary phenol:

$$C_6H_5NH_2+HNO_2=\underset{\text{Phenol.}}{C_6H_5(OH)}+N_2+H_2O.$$

The process actually takes place in two steps, as will be seen from the following experiment:

EXPT. 138.—Dissolve a few drops of aniline in excess of dilute hydrochloric acid (test with methyl-violet paper), cool the solution, and add a few drops of sodium nitrite solution. The liquid turns yellow, but no effervescence occurs. There is present diazobenzene chloride, which is very soluble in water:

$$C_6H_5NH_2.HCl+HNO_2=\underset{\substack{\text{Diazobenzene}\\\text{chloride.}}}{C_6H_5N_2.Cl}+2H_2O.$$

Divide the liquid into two parts, and warm one portion. Effervescence occurs and nitrogen is evolved. The smell of phenol, or carbolic acid, is then perceived.

$$C_6H_5N_2Cl+H_2O=\underset{\text{Phenol.}}{C_6H_5(OH)}+N_2+HCl.$$

Pour the other portion into a solution of phenol in caustic soda. A deep orange-red colour is at once produced. This is an **azo-colour**, the structure and properties of which will be described later (p. 277). The two reactions serve to identify a primary aromatic amino-compound.

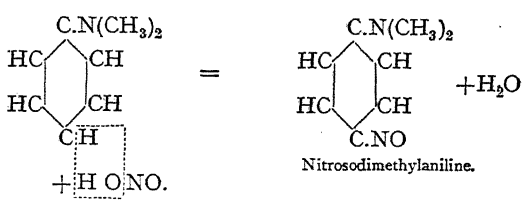
If nitrous acid is added to a secondary base, a nitrosamine

is formed, which is a yellow substance insoluble in water. Methylaniline yields nitrosomethylaniline—

$$\underset{\text{Methylaniline.}}{C_6H_5NH(CH_3)}+HNO_2=\underset{\text{Nitrosomethylaniline.}}{C_6H_5N(NO)CH_3}+H_2O.$$

EXPT. 139.—Dissolve a few drops of methylaniline in dilute hydrochloric acid, and add sodium nitrite solution as above. An emulsion consisting of fine drops of nitrosomethylaniline is formed, which may be removed by extraction with ether. On distilling the ether a yellow liquid remains, having a fragrant smell. If a few crystals of phenol are dissolved in strong sulphuric acid (2 c.c.) and a drop of nitrosomethylaniline is added, a blue colour is developed on warming, which changes to red on dilution with water. This reaction for "nitroso" compounds is known as **Liebermann's nitroso-reaction.** Together, the above two reactions serve to identify a secondary amino-compound.

In their behaviour with nitrous acid, the tertiary amino-compounds offer no analogy with the tertiary aliphatic amines. When nitrous acid is added to dimethylaniline, a deep red solution is obtained, from which orange crystals separate. This is the hydrochloride of a new base, nitrosodimethylaniline. The nitrous acid, here, attacks the nucleus:



Nitrosodimethylaniline.

EXPT. 140.—Dissolve a few drops of dimethylaniline in dilute hydrochloric acid. Notice that it is necessary to shake the mixture before a clear solution is obtained. Cool the liquid, and add cautiously a solution of sodium nitrite. Yellow crystals of the hydrochloride of the nitroso-compound soon begin to separate. If a portion of the liquid is made alkaline with caustic soda, a bright green precipitate is formed, which is the nitrosodimethylaniline base. It dissolves in ether with an emerald green colour.

Tertiary aromatic bases, like the aliphatic tertiary amines, combine with alkyl iodides and form quaternary ammonium

iodides (p. 203). Dimethylaniline, when warmed for a minute with methyl iodide, forms a crystalline trimethylphenylammonium iodide:

$$C_6H_5N(CH_3)_2+CH_3I=C_6H_5N(CH_3)_3I.$$
Trimethylphenylammonium iodide.

The primary and secondary bases do not yield compounds of this character.

Acetyl chloride, or acetic anhydride, may be used for distinguishing the primary and secondary from the tertiary bases. The primary and secondary amino-compounds form acetyl derivatives, but not the tertiary base.

Aniline and methylaniline give respectively acetanilide and methyl acetanilide:

$$C_6H_5NH_2+CH_3.COCl=C_6H_5NH.COCH_3+HCl.$$
Acetanilide.

$$C_6H_5NH(CH_3)+CH_3.COCl=C_6H_5N(CH_3)CO.CH_3+HCl.$$
Methylacetanilide.

EXPT. 141.—Add a few drops of acetyl chloride or acetic anhydride separately to aniline, methylaniline, and dimethylaniline. Warm for a minute over a small flame and pour into water. In the case of aniline and methylaniline, solid crystalline precipitates will be formed on rubbing with a glass rod, which are the acetyl derivatives of the two bases; but dimethylanilin is unchanged and remains liquid.

Diazo-compounds.—In 1860, Griess, a German chemist discovered what is known as the **diazo-reaction,** a process of fundamental importance, not only as an aid to organic synthesis among the aromatic compounds, but also as the source of a large class of artificial dye-stuffs, known as the **azo-dyes.** It has already been stated (p. 270) that if aniline is dissolved in hydrochloric acid and cooled, and sodium nitrite solution is then added, nothing is observable but a slight change in the colour of the solution which becomes yellow. A new substance is, however, present viz. the hydrochloride of a strong base. It is termed diazo benzene chloride, and the process is called **diazotising.**

The process is usually conducted by dissolving the equivalent

of one molecule of the base in two molecules of hydrochloric acid, and adding one molecule of sodium nitrite :

$$\begin{array}{l} C_6H_5N\!:\!H_2 \quad H\!:\!Cl \\ \quad +N\!:\!O \quad OH \end{array} = C_6H_5N_2.Cl + 2H_2O.$$

Diazobenzene chloride.

The group $C_6H_5N_2$ is a basic group which may be compared with ammonium, NH_4. Like ammonium, it does not exist in the free state, but forms a very unstable hydroxide, which is an oil, and a series of well-crystallised salts, which are extremely soluble in water, but not in alcohol or ether—

$C_6H_5N_2.OH$	$C_6H_5N_2.Cl.$	$C_6H_5N_2.NO_3.$	$C_6H_5N_2.SO_4H.$
Diazobenzene hydroxide.	Diazobenzene chloride.	Diazobenzene nitrate.	Diazobenzene sulphate.

All the salts, in the dry state, explode on heating, or by shock, especially the nitrate, which detonates violently with a slight blow. The formation of diazo-compounds is a property of the majority of the aromatic amino-compounds.

Structure of the Diazo-compounds.—The basic character of the diazo-group has suggested a formula, known as Blomstrand's formula, in which the nitrogen attached to the acid radical is pentavalent, as in the ammonium salts ; hence the compounds are sometimes called **diazonium** salts :

$$C_6H_5N{\equiv}N$$
$$|$$
$$Cl.$$

Blomstrand's formula.

Reactions of the Diazo-compounds.—Diazobenzene chloride may be taken as typical of the diazo-salts. It undergoes the following series of changes :

1. When boiled with alcohol, effervescence due to liberated nitrogen occurs. At the same time reduction of the phenyl group to benzene takes place at the expense of the alcohol, which loses hydrogen, and is oxidised to aldehyde :

$$\begin{array}{l} C_6H_5\!:\!N\!:\!Cl \\ \quad \| \\ +H\!:\!N\!:\!H \end{array} = C_6H_6 + N_2 + HCl.$$

An alkaline solution of stannous hydrate can also be used.

2. If the aqueous solution of diazobenzene chloride is boiled, nitrogen is evolved as before, and phenol is formed (p. 270):

$$\begin{matrix} C_6H_5.N.Cl \\ \| \\ OH.N.H \end{matrix} = C_6H_5(OH) + N_2 + HCl.$$

3. If a solution of potassium iodide is added to diazobenzene chloride and the mixture then warmed, the usual effervescence from escaping nitrogen occurs, and iodobenzene is formed:

$$C_6H_5N_2.Cl + K.I = C_6H_5I + N_2 + KCl.$$

In addition to the above, the following important reactions in which cuprous salts are employed should be noted. They are called, after their discoverer, **Sandmeyer's reactions,** but in what precise manner the changes occur is not very clear. It is certain that the copper salt forms an additive compound with the diazo-salt during the process.

If the diazo-salt is added to a solution of cuprous chloride in hydrochloric acid, to cuprous bromide in hydrobromic acid, or to cuprous cyanide in potassium cyanide, the following changes occur:

4. $C_6H_5N_2Cl + CuCl = C_6H_5Cl + N_2 + CuCl.$ (Chlorobenzene.)

5. $C_6H_5N_2Cl + CuBr = C_6H_5N_2Br + CuCl = C_6H_5Br + N_2.$ (Bromobenzene.)

6. $C_6H_5N_2Cl + CuCN = C_6H_5N_2CN + CuCl = C_6H_5CN + N_2.$ (Benzonitrile, or Phenylcyanide.)

The cuprous chloride, which is formed in each case, remains in solution.

All the above reactions may be carried out without isolating the diazo-salt.

EXPT. 142.—**Preparation of Chlorobenzene.**—Dissolve 40 grams of aniline in a mixture of 110 c.c. of concentrated hydrochloric acid and 80 c.c. of water and then cool quickly in a beaker, and stir so as to obtain small crystals. Place the beaker in ice and salt and

whilst it is cooling, prepare a solution of cuprous chloride. Dissolve 30 grams of copper carbonate in 300 c.c. of conc. hydrochloric acid, and boil with excess of copper turnings until a nearly transparent solution is obtained. The solution is decanted into a large round flask (2 litres) which is loosely corked, and placed in ice. Whilst this solution is cooling to 0° the diazobenzene chloride is prepared by adding the powdered sodium nitrite gradually to the aniline hydrochloride and stirring. The temperature should not rise above 10°. When three-quarters of the nitrite has been added, test occasionally with potassium iodide-starch paper until a drop gives an immediate deep blue or dark brown coloration. Add this solution gradually in portions of about 20 c.c. at a time to the cold solution of the cuprous chloride, and shake up well after each addition. After standing a short time the liquid is distilled in steam. The distillate is shaken up with a little caustic soda to remove phenol, and the chlorobenzene, which sinks to the bottom, is separated. The liquid is further extracted with a little chloroform, which is then added to the chlorobenzene, and the whole dehydrated with calcium chloride. The liquid is decanted, the chloroform distilled off and the residue collected at 125°–135°. The yield is about 30 grams.

EXPT. 143.—**Preparation of Iodobenzene.**—Mix together in a large round flask 25 grams of aniline with 25 c.c. of concentrated sulphuric acid in 200 c.c. of water and cool to 0° in a freezing mixture. Stir whilst cooling, to produce small crystals of the sulphate. Add slowly a solution of 18 grams of sodium nitrite in 40 c.c. of water, and if the temperature rises above 10°, add a few lumps of ice. When three-quarters of the nitrite solution has been added, test occasionally with potassium iodide–starch paper until a blue or brown stain is produced. Now add a solution of 45 grams of potassium iodide gradually, and, after well stirring, leave the mixture at the ordinary temperature for an hour, and then warm cautiously on the water-bath until effervescence ceases. The liquid is dark coloured, and a black oil settles to the bottom of the vessel. The oil consists of iodobenzene, and the dark colour of the solution is due to free iodine, which may be removed by the addition of a gram or two of sodium bisulphite. The mixture is now distilled in steam. The heavy oil, which is the iodobenzene, is removed with a tap-funnel, dehydrated over calcium chloride, poured off and distilled. It is a colourless liquid when pure and distils at 188°.

EXPT. 144.—**Preparation of Phenyl cyanide** (Benzonitrile).—Fifty grams of copper sulphate are dissolved in 200 c.c. of water

on the water-bath in a round flask (2 litres). Pure potassium cyanide (55 grams in 100 c.c. of water) is gradually added to the warm solution. The cuprous cyanide dissolves in excess of the potassium cyanide. As cyanogen gas is liberated the operation must be conducted in the fume cupboard :

$$2CuSO_4+4KCN=2CuCN+2K_2SO_4+(CN)_2.$$

The solution is left, whilst the aniline is diazotised. Eighteen grams of aniline are dissolved in 45 c.c. of concentrated hydrochloric acid diluted with 150 c.c. of water, cooled in ice, and well stirred. The mixture is kept cold whilst 16 grams of sodium nitrite in 40 c.c. of water is gradually added, until it gives an immediate coloration with potassium iodide–starch paper. The diazo-solution is then added in portions of about 10 c.c. at a time to the warm cuprous cyanide solution, with frequent shaking. A rapid effervescence occurs, nitrogen and some hydrocyanic acid being evolved. When, in the course of about fifteen minutes, the diazo-solution has been added, it is left on the water-bath until effervescence ceases ($\frac{1}{4}$ hour). The liquid turns a dark colour, and a black tarry deposit is formed. The product is distilled in steam. This should be carried out in the fume cupboard, as not only is hydrocyanic acid liberated, but also a small quantity of isocyanide, which is formed in the reaction, and produces an intolerable smell. The distillation is continued until no more yellow oil passes over. The phenyl cyanide is extracted with ether, dehydrated over calcium chloride and the ether distilled off on the water-bath. The yield is about 15 grams.

Phenylhydrazine, $C_6H_5.NH.NH_2$, is obtained by the reduction of diazobenzene chloride by means of stannous chloride, dissolved in hydrochloric acid :

$$C_6H_5N_2Cl+2SnCl_2+4HCl=\underset{\text{Phenylhydrazine hydrochloride.}}{C_6H_5NH.NH_2.HCl}+2SnCl_4.$$

The hydrochloride of phenylhydrazine is formed, from which caustic soda liberates the phenylhydrazine as an oil, which is extracted with ether.

Phenylhydrazine is extremely poisonous and care should be taken to keep it off the hands, especially if there is a cut or wound.

EXPT. 145.—**Preparation of Phenylhydrazine.**—Twenty grams of aniline are dissolved in 170 c.c. of concentrated hydrochloric acid and cooled to 0° in a freezing mixture. The solution of 20 grams

of sodium nitrite in 100 c.c. of water is gradually added, the temperature being kept below 10°, until a drop of the mixture, diluted with water, turns potassium iodide–starch paper blue. To the mixture, still cooled in ice, 120 grams of stannous chloride, dissolved in about an equal weight of concentrated hydrochloric acid, is added. A thick white crystalline precipitate of phenylhydrazine hydrochloride separates. It is allowed to stand for half an hour and filtered at the pump ; it is then separated as far as possible from the mother liquor, and transferred to a flask. The free base is obtained by decomposing the hydrochloride with caustic soda. An excess of caustic soda is added and the mixture well shaken. The free base, which separates as a reddish coloured oil, is ex-

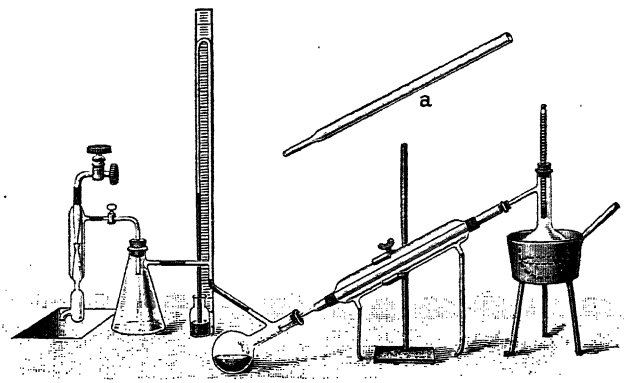


FIG. 62.—Apparatus for distillation under reduced pressure.

tracted with ether, and the ethereal solution dehydrated over solid potassium carbonate. The ether is then removed on the water-bath, and the residual oil either used without further purification or distilled under reduced pressure. The yield is 15–20 grams.

The apparatus for distillation at reduced pressure is shown in Fig. 62. The flask is heated in an oil or paraffin-bath. The condenser tube is shown at *a*. It is an ordinary tube, but has a narrower piece fixed on to the end to fit into the neck of a second distilling flask. The remainder of the apparatus needs no explanation. Before heating the liquid it is advisable to introduce some bits of porous pot.

The Azo-colours.—This important group of dyes is obtained by adding the solution of a diazo-salt to an aromatic amino- or

hydroxy-compound, or to a derivative, usually the sulphonic acid. The following experiments will illustrate the process.

EXPT. 146.—Dissolve a few drops of aniline in excess of dilute hydrochloric acid, and convert it into the diazo-salt by adding sodium nitrite solution in the usual way.

1. Pour a portion of the liquid into a solution of dimethylaniline in a little dilute hydrochloric acid. On the addition of caustic soda solution the yellow azo-colour is formed, which changes to the pink hydrochloride on the addition of hydrochloric acid:

$$C_6H_5N_2Cl + C_6H_5N(CH_3)_2 = C_6H_5N{:}N.C_6H_4N(CH_3)_2.HCl.$$

Dimethylaminoazobenzene hydrochloride.

2. Add another portion of the diazo-salt solution to ordinary phenol dissolved in caustic soda. An orange colour is produced from the formation of the sodium salt of the hydroxyazo-compound:

$$C_6H_5N_2.Cl + C_6H_5(ONa) = C_6H_5N{:}NC_6H_4(ONa) + HCl.$$

Sodium hydroxyazobenzene.

3. A derivative of an amino-compound may be used as the compound to be diazotised in place of a simple base like aniline. Diazotise sulphanilic acid (aniline *p*-sulphonic acid) with hydrochloric acid and sodium nitrite in the same way as aniline, taking care to avoid an excess of the nitrite. Add the solution to dimethylaniline dissolved in hydrochloric acid. The red colour is the free sulphonic acid of the azo-colour. The sodium salt is precipitated in orange crystals on adding caustic soda, and is known as **methyl-orange**, **helianthin**, or sometimes as **tropæolin**, which changes to the red hydrochloride on adding hydrochloric acid:

$$SO_3H.C_6H_4N_2.Cl + C_6H_5N(CH_3)_2 = SO_3H.C_6H_4N{:}N.C_6H_4N(CH_3)_2 + HCl.$$

Methyl-orange.

QUESTIONS ON CHAPTER XXI

1. Describe and explain the process of steam distillation. How is it applied in the preparation of aniline? What other method could be used on a small scale for separating the aniline?

2. What reagents are usually employed for reduction of nitro-compounds to amino-compounds? Illustrate their use in reference to dinitrobenzene.

3. What are the principal reactions which distinguish aniline and its homologues from ethylamine and its homologues ?

4. How is dimethylaniline prepared from benzene ? Compare and contrast the behaviour of fatty and aromatic amines towards nitrous acid.

5. Describe the action of reagents on the primary, secondary and tertiary amino-compounds.

6. What is the action of the following reagents on aniline : (1) sodium hypochlorite, (2) potassium dichromate and sulphuric acid, (3) the mineral acids, (4) the halogens ?

7. What is acetanilide, how is it prepared, and for what purpose is it used ? In what respects does it resemble acetamide ?

8. What is the " diazo " reaction ? Indicate how it is applied to the preparation of hydrocarbons, phenols, nitriles (cyanides), and halogen substitution-products respectively.

9. By what process can acetylene be converted into benzene and benzene into phenol ?

10. Calculate the quantity of hydrochloric acid and sodium nitrite required to convert 20 grams of aniline into phenol, and the theoretical amount of product obtainable.

11. What are Sandmeyer's reactions ? Give some details of the preparation of chlorobenzene from aniline by Sandmeyer's reaction.

12. Describe the preparation of a solution of diazobenzene chloride. Explain what happens if (1) potassium iodide, (2) cuprous chloride are added, and (3) the aqueous solution boiled.

13. How is phenylhydrazine obtained ? Give a brief account of its use as a reagent.

14. What is an *azo-colour* ? Illustrate the formation by the action of diazotised sulphanilic acid on phenol.

CHAPTER XXII

THE PHENOLS

Phenols.—The name is given to the hydroxy-derivatives of the aromatic hydrocarbons, in which the hydrogen of the nucleus is replaced by hydroxyl. The simplest member of the group is ordinary phenol, or carbolic acid, $C_6H_5(OH)$. It is called a **monohydric** phenol, by which is meant a phenol with one hydroxyl group, and conveys the same idea as monohydric applied to ethyl alcohol (p. 139). If more than one hydrogen atom in benzene is replaced by hydroxyl, the compounds are known as di- and trihydric phenols, etc.:

$C_6H_4(OH)_2$.	$C_6H_3(OH)_3$.
Dihydric phenol.	Trihydric phenol.

Structurally, the phenols are analogous to the alcohols, but, as the name carbolic acid implies, they possess a distinctly acid character, inasmuch as they form salts with metallic hydroxides. Ordinary phenol, though sparingly soluble in water, dissolves readily in caustic soda, and, on evaporating the solution, yields a solid sodium compound. This is sodium phenate or carbolate, $C_6H_5(ONa)$.

EXPT. 147.—Add a few c.c. of water to a few grams of ordinary phenol. Little of the phenol dissolves; but the addition of caustic soda rapidly effects solution. Divide the solution into two parts and add dilute sulphuric acid to one and pass carbon dioxide through the other portion. Provided the solution is sufficiently concentrated, phenol will be precipitated as an oil from both solutions.

Sources of the Phenols.—Many of the phenols are formed by the destructive distillation of organic matter, *e.g.* wood and coal. Wood-tar and coal-tar are rich in phenols, coal-tar being the main source of ordinary phenol. There are two synthetic methods for the preparation of phenol; first the fusion of the sulphonate with caustic alkali:

$$C_6H_5SO_3Na+NaOH=C_6H_5(OH)+Na_2SO_3.$$

and second the decomposition of diazo-salts with water (p. 274):

$$C_6H_5N_2Cl+H_2O=C_6H_5(OH)+N_2+HCl.$$

EXPT. 148.—**Preparation of Phenol from Sodium benzene-sulphonate.**—Dissolve 35 grams of caustic soda in the smallest quantity of water (5 c.c.) by heating in a silver or nickel basin or crucible and add 20 grams of powdered sodium benzene-sulphonate (p. 253). The temperature of the melt, which during the process is kept constantly stirred, must not exceed 250°. It is convenient to use the thermometer as stirrer, the bulb and part of the stem being encased in a glass tube closed at one end. When the requisite temperature has been reached, a small flame is sufficient to maintain it. The mass is first thick and pasty, but soon becomes semi-fluid and remains in this condition, gradually changing in colour from yellow to brown. Towards the end of the operation (one hour) it regains somewhat its original consistency. On cooling, the melt is dissolved in a little water and the alkaline reddish-brown liquid (sodium phenate and excess of alkali) acidified with concentrated hydrochloric acid in the cold. Phenol separates out as a light yellow oil, which is extracted three times with ether. The ethereal solution dehydrated over anhydrous sodium sulphate is distilled, first on the water-bath until the ether is removed, and then over the flame. The portion boiling at 175°–185° is nearly pure phenol. It distils as a colourless liquid and solidifies at once on cooling and melts at 42°. The yield is 6–7 grams. A solution in water gives a violet coloration with ferric chloride and a white precipitate of tribromophenol with bromine water.

EXPT. 149.—**Preparation of Phenol from Aniline.**—Dissolve 25 grams of aniline in a mixture of 13 c.c. of concentrated sulphuric acid and 500 c.c. of water and cool to the ordinary temperature. A solution of 18 grams of sodium nitrite in 40 c.c. of water is gradually added. The clear liquid is then gently warmed on the water-bath until the evolution of nitrogen ceases. The

solution, which has become very dark coloured, is distilled in steam until the distillate produces only a slight precipitate with bromine water. A small quantity of tarry residue remains. The distillate is then extracted three times with small quantities (50 c.c.) of ether. The ethereal solution is dehydrated over anhydrous sodium sulphate, filtered, and the ether removed on the water-bath. The phenol is then distilled over the flame with a condenser tube, and collected at 180°–185°. The distillate solidifies on cooling. The yield is 10–15 grams.

Ordinary Phenol, Carbolic acid, Phenic acid, Hydroxybenzene, $C_6H_5(OH)$.—Phenol was discovered by Runge in 1834 in coal-tar, which is the present source of the substance. The middle or carbolic oil (p. 247), obtained in the distillation of coal-tar, contains the greater part of the phenol. It is shaken up with just sufficient caustic soda solution to dissolve the phenol. The alkaline liquid is then removed from the undissolved oil, which is subsequently worked up for naphthalene (p. 304) and acidified with sulphuric acid. The crude phenol separates on the surface as a dark-coloured oil, and, after standing, is carefully removed and distilled. The distillate constitutes the crude carbolic acid of commerce. In order to obtain the colourless crystals of the pure substance, the crude carbolic acid is fractionated, when the greater part of the distillate solidifies on cooling or freezing, and any residual liquid is drained off. One ton of coal yields about 1½ lb. of phenol.

Phenol forms large, colourless crystals, which melt at 42° and boil at 183°. On exposure to air and light it turns a pink colour. Phenol has the well-known smell associated with sanitary disinfecting preparations, for which it is largely used. Carbolic powders are made by mixing phenol with a variety of ingredients, such as china clay, etc. Pure phenol has a strongly corrosive action on the skin, producing sores which heal with difficulty. A very dilute solution (3 per cent.) is therefore used for washing wounds or cleansing the skin. Taken internally it acts as a strong poison.

Phenol is used in the manufacture of **salicylic acid** (p. 297), **picric acid** (p. 283), **phenacetin** (p. 283), and for other purposes.

Nitrophenols.—Strong nitric acid attacks phenol vigorously and forms resinous products. In order to obtain the mono-

nitro-derivatives, the nitric acid is somewhat diluted with water and the phenol is slowly added. Both ortho- and para-nitrophenols are formed.

EXPT. 150.—**Preparation of *o*- and *p*-Nitrophenol.**—Mix 50 c.c. of concentrated nitric acid with 170 c.c. of water and gradually add 40 grams of melted phenol; cool in water and shake well after each addition. On the addition of the phenol, the liquid immediately changes to a deep brown or black colour, and a heavy dark-brown oil separates out. When the phenol has been added, the mixture is allowed to stand for 12 hours. The oil has by that time collected at the bottom of the vessel, and may be freed from acid by decanting and pouring in fresh water three or four times. The contents of the flask consist of nearly equal quantities of para- and ortho-nitrophenols mixed with resinous products. In order to separate the two isomers, the product is distilled in a current of steam (Fig. 61, p. 263) until the distillate is almost colourless. The ortho-compound distils in the form of a yellow oil, which may solidify in the condenser, in which event the water is temporarily run out of the condenser. The solid in the receiver is separated by filtration and dissolved in spirit at 40°, to which water is then added, drop by drop, until a turbidity is produced. The yield is 15 grams of sulphur-yellow needles, m.p. 45°. The solid residue contains the para-compound mixed with black, resinous substances, from which it is separated by repeatedly extracting with boiling water. The united portions of the aqueous extract are boiled with animal charcoal for half an hour in a large basin, and filtered through a fluted filter moistened with water. The filtrate is made alkaline with caustic soda solution, and concentrated to a small bulk (100 c.c.). If tarry matter separates, it must be filtered through a wet filter. To obtain the free para-compound, the concentrated aqueous solution of the sodium salt is cooled, and the separated sodium salt filtered. The crystals are dissolved and acidified with concentrated hydrochloric acid, and the nitrophenol, which separates, is filtered and recrystallised from hot water. The yield is 10 grams. It crystallises in colourless needles, m.p. 114°.

$$\underset{\text{Phenol.}}{C_6H_5OH} + HONO_2 = \underset{\text{Nitrophenol.}}{HOC_6H_4NO_2} + H_2O.$$

p-Nitrophenol is used in the preparation of **phenacetin**, or *p*-acetaminophenyl ether, $C_2H_5O.C_6H_4.NHCOCH_3$.

Picric acid, 2:4:6-Trinitrophenol, $C_6H_2(OH)(NO_2)_3$, is the final product of the direct nitration of phenol, and is also formed

when nitric acid acts on many organic substances, such as silk, wool, leather, etc.

In the manufacture of picric acid, phenolsulphonic acid is nitrated in place of phenol, and the formation of tarry and resinous by-products is thereby avoided.

Phenolsulphonic acid is obtained by warming phenol with sulphuric acid on the water-bath (both ortho- and para-sulphonic acids are formed, the ortho-compound predominating when the action occurs at a low temperature, and becoming gradually transformed into the para-compound at 100°). The phenolsulphonic acid is then added slowly to strong nitric acid and subsequently heated:

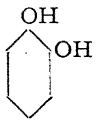
$$\underset{\text{Phenolsulphonic acid.}}{C_6H_4(OH)SO_3H}+3HNO_3=\underset{\text{Picric acid.}}{C_6H_2(OH)(NO_2)_3}+H_2SO_4+3H_2O.$$

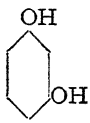
EXPT. 151.—**Preparation of Picric acid.**—Twenty-five grams of phenol and 14 c.c. of concentrated sulphuric acid are heated together in a porcelain basin for a few minutes, until a clear solution of phenol sulphonic acid is obtained. It is diluted with half its volume of water, then well cooled, and slowly added, in small quantities at a time, from a tap-funnel, to 70 c.c. of concentrated nitric acid contained in a flask (1 litre), and well shaken. The liquid assumes a deep red colour, a considerable rise of temperature occurs, and red fumes are evolved. When the phenol sulphonic acid has been added, the flask is placed on the water-bath and heated, with the addition of 20 c.c. of fuming nitric acid, for 1–2 hours. On cooling, picric acid separates out as a yellow, crystalline mass. It is diluted with water, filtered at the pump, and washed free from the mother liquor with cold water. It is then purified by recrystallisation from a large quantity of hot water acidified with a few drops of sulphuric acid. The yield is about 30 grams. It forms yellow crystals which melt at 122°.

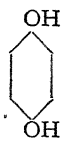
Picric acid is a strong acid which explodes violently on detonation and is used in the explosives known as **lyddite** and **melinite.** It is a strong acid and forms a series of salts many of which explode on heating and on percussion. Picric acid is also used as a yellow dye.

The **cresols** are hydroxy-toluenes, $CH_3.C_6H_4.OH$, and occur in the higher boiling fractions of coal-tar phenol.

The dihydroxybenzenes exist in three isomeric forms; the ortho-compound is called **catechol**, the meta, **resorcinol**, and the para, **quinol**:


Catechol.


Resorcinol.


Quinol.

Catechol, $C_6H_4(OH)_2$, was originally obtained by distilling **catechu** (the extract of the Indian *Acacia catechu*), and by fusing certain natural resins with potash. It is also prepared from *o*-phenolsulphonic acid by fusing the potassium salt with potash:

$$\underset{\text{Potassium-}o\text{-phenol-sulphonate.}}{C_6H_4(OH)SO_3K} + KOH = \underset{\text{Catechol.}}{C_6H_4(OH)_2} + K_2SO_3.$$

The best method, however, is to oxidise *o*-hydroxybenzaldehyde with an alkaline solution of hydrogen peroxide:

$$C_6H_4(OH).CHO + H_2O_2 = \underset{\text{Catechol.}}{C_6H_4(OH)_2} + \underset{\text{Formic acid.}}{H.CO_2H}.$$

Catechol crystallises in colourless plates which melt at 104°. It gives with ferric chloride a green coloration, which changes to red on the addition of sodium bicarbonate solution. This reaction is characteristic of all ortho-dihydric phenols. Catechol reduces Fehling's solution.

Resorcinol, $C_6H_4(OH)_2$.—Resorcinol can be obtained by a variety of synthetic methods. The industrial process is to fuse the sodium salt of *m*-benzenedisulphonic acid (p. 252) with caustic soda:

$$\underset{\text{Sodium-}m\text{-benzene-disulphonate.}}{C_6H_4(SO_3Na)_2} + 2NaOH = \underset{\text{Resorcinol.}}{C_6H_4(OH)_2} + 2Na_2SO_3.$$

Resorcinol crystallises in colourless needles which melt at 119°. It has a sweetish taste, and is very soluble in water. The reactions of resorcinol resemble those of phenol.

Resorcinol is used in the preparation of fluorescein, which dissolves in dilute caustic alkalis and in alcohol with a brilliant green fluorescence.

EXPT. 152.—Heat together over a small flame about 0·25 gram of phthalic anhydride (p. 301) and 0·5 gram of resorcinol for a minute, taking care not to raise the temperature too high. It is advisable to hold the test-tube a little above the flame. Let the mixture cool, dissolve it in a little caustic soda solution, and pour it into water. The liquid shows a brilliant green fluorescence.

Quinol, Hydroquinone, $C_6H_4(OH)_2$.—Quinol is occasionally found among vegetable substances. It is present in bearberry in combination with glucose, as the glucoside, **arbutin.** It is usually obtained from quinone, $C_6H_4O_2$ (see below), by reduction with sulphurous acid, and extraction with ether:

$$\underset{\text{Quinone.}}{C_6H_4O_2} + H_2O + H_2SO_3 = \underset{\text{Quinol.}}{C_6H_6O_2} + H_2SO_4.$$

EXPT. 153.—Dissolve a few of the yellow crystals of quinone in water, and pass in sulphur dioxide. The quinone is reduced. Extract with a little ether and decant the ethereal solution on to a watch-glass. On evaporation, colourless crystals of quinol are deposited.

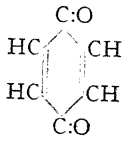
Quinol is readily oxidised to quinone by ferric chloride and other oxidising agents.

EXPT. 154.—Dissolve a few crystals of quinol in water, and add a few drops of ferric chloride. The solution turns yellow and contains quinone. The dirty-green coloration, which is observed on first adding the ferric chloride, is due to the formation of a compound of quinol and quinone, known as **quinhydrone,** $C_6H_4O_2.C_6H_4(OH)_2$. Extract with ether as in Expt. 153.

Quinol crystallises in colourless needles which melt at 169°. It is very soluble in water, and its reducing properties in alkaline solution render it a useful photographic developer.

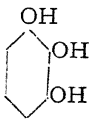
Quinone, $C_6H_4O_2$, was originally obtained by the oxidation of quinic acid (p. 319), which is found in cinchona bark associated with the cinchona alkaloids (p. 319), but has chemically no connection with the alkaloid, quinine. It is formed when quinol is oxidised; but it is usually prepared by the oxidation of aniline in the cold, with potassium dichromate and sulphuric acid. The dark product is extracted with ether, which dissolves the quinone, and on removing the ether, benzoquinone crystallises in golden-yellow prisms, which melt at 116° and sublime without

decomposition, emitting a peculiar smell and acrid vapours. It is represented as a diketone :

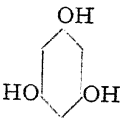


Quinone.

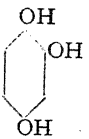
The three trihydroxybenzenes have the following structural formulæ and names :



Pyrogallol.



Phloroglucinol.



1 : 2 : 4-Trihydroxybenzene.

Pyrogallol, Pyrogallic acid, $C_6H_3(OH)_3$.—Pyrogallol was first obtained by Scheele in 1786 by heating gallic acid, and the process is still used for its preparation. When gallic acid is heated it loses carbon dioxide :

$$\underset{\text{Gallic acid.}}{C_6H_2(OH)_3CO_2H} = \underset{\text{Pyrogallol.}}{C_6H_3(OH)_3} + CO_2.$$

Pyrogallol melts at 132° and is very soluble in water. In alkaline solution it rapidly absorbs oxygen and darkens in colour. Among the products of oxidation, acetic acid, carbon dioxide, and a little carbon monoxide have been detected. The property is utilised in gas analysis for estimating oxygen.

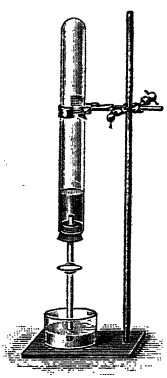


Fig. 63.

Expt. 155.—Take a long tube closed at one end and furnished with a cork holding a glass tap (Fig. 63). Introduce a few grams of pyrogallol, and then fill the tube with oxygen from a cylinder. Quickly introduce a little solution of caustic soda, close the tube and shake for a minute. On opening the tap under water, water rapidly ascends the tube, indicating absorption of oxygen gas.

Pyrogallol reduces gold, silver, and mercury solutions, and is extensively used as a photographic developer.

QUESTIONS ON CHAPTER XXII

1. Explain the meaning of the term *phenol*. Compare and contrast amyl alcohol and ordinary phenol.

2. Give examples of mono-, di-, and tri-hydric phenols. Name any properties by which a phenol may be distinguished from a member of any of the previous groups of compounds, and devise a method for separating ordinary phenol from (1) benzene, (2) chlorobenzene, (3) nitrobenzene, and (4) aniline.

3. Give a list of the natural sources of the phenols, and describe the preparation of carbolic acid from coal-tar.

4. In what manner may the phenols be obtained from the hydrocarbons? Mention two methods.

5. Describe a method for separating the phenols from organic acids. Illustrate this in the case of a mixture of acetic acid and carbolic acid.

6. How can phenol be (1) obtained from benzene and aniline; and (2) converted into benzene and aniline? Describe the action of the following reagents on phenol: (1) caustic soda, (2) bromine, (3) phosphorus pentachloride, (4) nitric acid, (5) sulphuric acid, and (6) acetyl chloride.

7. How are the two mononitrophenols obtained? How are the ortho- and para-compounds distinguished, and for what purpose is the para-compound employed?

8. Describe the preparation of picric acid. Why is it termed an acid? Compare it with carbolic acid. What are its technical uses?

9. How is pyrogallol obtained? For what purpose is it used? What is its structural formula?

10. What is the relation of quinol to quinone? How can they be converted into one another and how can they be distinguished?

CHAPTER XXIII

THE AROMATIC ALCOHOLS, ALDEHYDES, AND ACIDS

Benzyl alcohol, $C_6H_5.CH_2(OH)$, is an example of an aromatic alcohol and is isomeric with the cresols. It is found in Peru and Tolu balsam and in storax (the exudation from *Styrax officinalis*, a shrub which grows in the East) as the benzyl ester of benzoic and cinnamic acids.

Benzyl alcohol is most easily prepared by boiling benzyl chloride with a solution of potassium carbonate, until the pungent smell of the chloride vanishes :

$$2C_6H_5.CH_2Cl+K_2CO_3+H_2O=2C_6H_5.CH_2(OH)+2KCl+CO_2.$$
Benzyl alcohol.

EXPT. 156.—**Preparation of Benzyl alcohol.**—In a round flask ($\frac{1}{2}$ litre) attached to a reflux condenser, boil over wire-gauze a mixture of 20 grams of benzyl chloride and 16 grams of potassium carbonate in 200 c.c. of water with the addition of a few bits of porous pot. The boiling must be continued until the smell of benzyl chloride has disappeared (6–8 hours). Extract the liquid with ether, dehydrate over potassium carbonate, decant through a filter and distil off the ether on the water-bath. Continue the distillation over wire-gauze, run the water out of the condenser and collect at 200°–210°. The yield is 12–15 grams. On warming with strong hydrochloric acid it is converted into benzyl chloride (compare ethyl alcohol and hydrochloric acid) :

$$C_6H_5CH_2OH+HCl=C_6H_5CH_2Cl+H_2O.$$

Benzaldehyde, Oil of Bitter Almonds, $C_6H_5.CHO$.—Few compounds have played so important a *rôle* in the development of organic chemistry as benzaldehyde, whether we consider it historically, as affording by its chemical changes the first clear

conception of the term compound radical (p. 38), or chemically, as marking the rapid progress of synthetic organic chemistry.

Benzaldehyde was originally obtained from bitter almonds, in which, as Wöhler showed, it is present as the glucoside, **amygdalin** (p. 209). When amygdalin is boiled with dilute acids, it is hydrolysed and yields benzaldehyde, hydrocyanic acid, and glucose. The same change occurs if the almonds are crushed in a mortar with a few drops of water. In the second case, the ferment **emulsin** which is present in the almonds is the hydrolytic agent. The benzaldehyde may be removed by distilling in steam, and purified by the method described below.

EXPT. 157.—Grind up a few bitter almonds with a little water in a mortar, and leave them for half an hour. The smell of the aldehyde and of hydrocyanic acid will be perceived.

Benzaldehyde is prepared by the oxidation of benzyl alcohol or by distilling a mixture of calcium benzoate and calcium formate (p. 66):

$$\begin{matrix}(C_6H_5CO_2)_2Ca \\ +(HCO)_2Ca\end{matrix} = \underset{\text{Benzaldehyde.}}{2C_6H_5CHO} + 2CaCO_3.$$

It is conveniently prepared from benzyl chloride.

EXPT. 158.—**Preparation of Benzaldehyde.**—The mixture of 50 grams of benzyl chloride, 40 grams of copper nitrate in 500 c.c. of water is heated to boiling in a round flask (1½ litres) with reflux condenser on the sand-bath for a day (8–9 hours). A slow current of carbon dioxide is at the same time passed through the liquid to prevent oxidation of the benzaldehyde by absorption of oxygen from the air. During the process nitrous fumes are slowly evolved. When the reaction is complete, the contents of the flask are extracted with ether, and the yellow oil remaining, after distilling off the ether, is well shaken with a saturated solution of sodium bisulphite and allowed to stand for a time. The colourless crystalline mass which separates is filtered, washed with a little alcohol and ether, and then drained on a porcelain filter. The aldehyde is regained by adding dilute sulphuric acid in excess and distilling in steam. The distillate is extracted with ether, dehydrated over calcium chloride, decanted, and the ether distilled off. The yield is about 15 grams.

$$2C_6H_5CH_2Cl + Cu(NO_3)_2 = 2C_6H_5COH + CuCl_2 + 2HNO_2.$$

It is manufactured on a large scale from benzal chloride by heating it with milk of lime, under pressure, in an iron vessel:

$$C_6H_5CHCl_2 + H_2O + CaO = C_6H_5CHO + CaCl_2 + H_2O.$$

Benzaldehyde can be readily purified by converting it into the crystalline bisulphite compound, which is washed with ether to remove impurities, and then decomposed with dilute sulphuric acid in a current of steam:

$$C_6H_5CH(OH)SO_3Na + H_2SO_4 = C_6H_5CHO + Na_2SO_4 + H_2O + SO_2.$$

EXPT. 159.—Shake up a few c.c. of benzaldehyde with an equal volume of a strong solution of sodium bisulphite. It immediately solidifies to a mass of crystals of the bisulphite compound.

Properties of Benzaldehyde.—Benzaldehyde is a colourless liquid, which boils at 179° and possesses a fragrant smell of bitter almonds. It quickly oxidises on exposure to the air and forms benzoic acid. A bottle of benzaldehyde will generally contain crystals of benzoic acid in the neck.

Benzaldehyde gives Schiff's reaction (p. 50). It very slowly reduces ammonia-silver nitrate, and alkaline copper solution, a fact which may be in part accounted for by its insolubility in water. It forms a bisulphite compound described in Expt. 159, and a cyanhydrin with hydrocyanic acid:

$$C_6H_5CHO + HCN = C_6H_5CH(OH)CN.$$

Benzaldehyde cyanhydrin.

With phenylhydrazine, benzaldehyde forms a phenylhydrazone, $C_6H_5CH{:}N.NHC_6H_5$.

EXPT. 160.—Make a dilute solution of phenylhydrazine acetate (p. 51), and add it to a drop of benzaldehyde. A yellow, crystalline precipitate of the hydrazone is thrown down.

With hydroxylamine, benzaldehyde yields benzaldoxime, $C_6H_5CH{:}N.OH$.

$$C_6H_5CHO + H_2NOH = C_6H_5.CH{:}NOH + H_2O.$$

Benzaldoxime.

So far benzaldehyde exhibits a close correspondence with the aliphatic aldehydes. It is distinguished from them by its behaviour with ammonia, and the caustic alkalis. When strong

ammonia solution is added to benzaldehyde, a crystalline compound is gradually deposited, which is not an aldehyde-ammonia, but a substance known as **hydrobenzamide**, which is formed as follows:

$$3C_6H_5CHO + 2NH_3 = \underset{\text{Hydrobenzamide}}{(C_6H_5CH)_3N_2} + 3H_2O.$$

EXPT. 161.—Add 5 c.c. concentrated ammonia to 1 c.c. benzaldehyde, cork up and leave two days. Crystals of hydrobenzamide will be deposited.

Caustic potash breaks up benzaldehyde into a mixture of benzyl alcohol and potassium benzoate. Two molecules of benzaldehyde take part in the reaction, one molecule being oxidised to benzoic acid at the expense of the other, which is reduced to benzyl alcohol:

$$\begin{array}{l} C_6H_5CHO + C_6H_5CHO \\ \quad + \ OK \qquad H \end{array} = \underset{\text{Potassium benzoate.}}{C_6H_5CO_2K} + \underset{\text{Benzyl alcohol.}}{C_6H_5.CH_2(OH)}.$$

EXPT. 162.—Shake up together 10 grams of benzaldehyde with 9 grams caustic potash in 6 c.c. of water until a permanent emulsion is formed, and let it stand 3–4 hours. Dissolve the solid product in a little water and shake out with ether twice. On acidifying the aqueous portion with hydrochloric acid, benzoic acid is precipitated. Filter and wash with a little cold water and dry. Distil the ether from the ethereal solution. The residue is benzyl alcohol.

The Aromatic acids derive their properties as acids from the presence of the carboxyl group, which may be either in the nucleus or side-chain of the aromatic compound. The isomers, toluic and phenylacetic acid are examples of the two classes of compounds:

$\underset{\text{Toluic acid.}}{(CH_3)C_6H_4.CO_2H.}$ $\qquad$ $\underset{\text{Phenylacetic acid.}}{C_6H_5.CH_2.CO_2H.}$

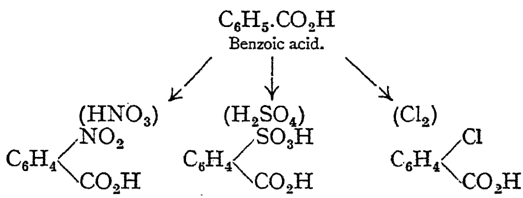
The general properties of both classes resemble those of the aliphatic acids. They form salts with metals, esters with the alcohols and acid chlorides, anhydrides, and amides by similar methods. The following derivatives of benzoic acid may be taken

by way of illustration, by the side of which the corresponding derivatives of acetic acid are placed for comparison:

$C_6H_5.CO.ONa$	Sodium benzoate.	$CH_3.CO.ONa$	Sodium acetate.
$C_6H_5.CO.OC_2H_5$	Ethyl benzoate.	$CH_3.CO.OC_2H_5$	Ethyl acetate.
$C_6H_5.CO.Cl$	Benzoyl chloride.	$CH_3.CO.Cl$	Acetyl chloride.
$C_6H_5.CO$ >O $C_6H_5.CO$	Benzoic anhydride.	$CH_3.CO$ >O $CH_3.CO$	Acetic anhydride.
$C_6H_5.CO.NH_2$	Benzamide.	$CH_3.CO.NH_2$	Acetamide.

Any difference in properties between the aromatic and aliphatic acids may generally be ascribed (1) to the larger proportion of carbon to carboxyl in the aromatic acids, which decreases the solubility in water; (2) to the higher molecular weight, which renders the substance less volatile (the aromatic acids are crystalline solids); (3) to the presence of the benzene nucleus, which increases the strength of the acid.

The aromatic acids, like the hydrocarbons, are acted upon by chlorine, bromine, and nitric and sulphuric acids, and give substitution products from which amino-acids, hydroxy-acids, and other derivatives may be obtained by means of the reactions already studied.



Nitrobenzoic acid. Sulphobenzoic acid. Chlorobenzoic acid.

By replacing more than one hydrogen atom by carboxyl, either in the nucleus or side-chain, polybasic acids are obtained. Examples of dibasic acids are the three phthalic acids (p. 259). The carboxyl is readily replaced by hydrogen by distilling the acid (or its calcium salt) with lime or, in some cases, by the action of heat alone. An example of the first is benzoic acid, which gives benzene on distillation with lime (p. 242); of the

second, gallic acid, which loses carbon dioxide on simply heating, forming pyrogallol (p. 287).

Many of the acids are found in nature as constituents of plants and, occasionally, of animal products. As a rule, they are more readily prepared by one or other of the numerous synthetic methods, which are described under benzoic acid.

Benzoic acid, $C_6H_5.CO_2H$, has long been known, and was originally obtained by heating gum-benzoin, a resin obtained by incisions made into the stem of *Styrax benzoin*, a tree which is indigenous to Sumatra and Java. The true composition of benzoic acid was determined by Liebig and Wöhler in 1832. They discovered some of the derivatives enumerated above (p. 289) and many others, and showed that the same group of elements, C_7H_5O (now written, C_6H_5CO), which they termed *benzoyl*, ran through the whole series of compounds. These were the facts which they embodied in their classical research on "The Radical of Benzoic Acid," wherein they placed the theory of the compound radical for the first time on a secure foundation.

EXPT. 163.—The formation of benzoic acid from gum-benzoin is readily shown as follows: Place a little of the resin in a porcelain basin, cover it with a cone made out of filter paper, and heat the basin gently on a sand-bath over a small flame. The resin fuses, and crystals of benzoic acid sublime into the paper cone, emitting a smell resembling incense.

Benzoic acid is present in the resin chiefly in the form of the ester of benzyl alcohol. A small amount of the same ester is also found in Peru and Tolu balsam. Another source of benzoic acid is **hippuric acid,** which is present in the urine of horses and cattle and other herbivorous animals, and has already been referred to under glycine (p. 233).

Preparation of Benzoic acid.—Benzoic acid is obtained by the following general synthetic methods, which may be applied to the preparation of other acids of the series:

1. By hydrolysis of phenyl cyanide, or benzonitrile, usually by boiling with moderately strong sulphuric acid (p. 78):

$$\underset{\text{Benzonitrile.}}{C_6H_5CN} + 2H_2O = \underset{\text{Benzoic acid.}}{C_6H_5.CO_2H} + NH_3.$$

As the cyanides are easily obtained from the amino-compounds by means of the diazo-reaction, the method is available both for preparing the acid and its derivatives.

EXPT. 164.—Add 4 c.c. of water to 6 c.c. of concentrated sulphuric acid and to the mixture add about 2 grams of phenyl cyanide (p. 275) and boil gently until the oily drops disappear. On adding a little water and cooling benzoic acid crystallises.

2. By the oxidation of aromatic compounds containing one side-chain, and even more readily if the side-chain is substituted. Toluene can be oxidised to benzoic acid by heating it with dilute nitric acid in a sealed tube; but if benzyl chloride, benzyl alcohol, or benzaldehyde is taken, the reaction is facilitated, and boiling with potassium permanganate is sufficient to effect oxidation.

The reaction with benzyl chloride probably occurs in two steps:

1. $2C_6H_5CH_2Cl+Na_2CO_3+H_2O=2C_6H_5CH_2OH+2NaCl+CO_2$.

2. $3C_6H_5CH_2OH+4KMnO_4=3C_6H_5CO_2K+4MnO_2+KOH+4H_2O$.

EXPT. 165.—**Preparation of Benzoic acid.**—Five grams of benzyl chloride and 4 grams of anhydrous sodium carbonate in 50 c.c. of water are mixed in a round flask ($\frac{1}{2}$ litre) attached to a reflux condenser, and boiled gently over wire-gauze, whilst a solution of 8·5 grams of potassium permanganate in 150 c.c. of water is gradually dropped in from a tap-funnel pushed through the top of the condenser. In the course of 2–3 hours the pink colour of the permanganate will have vanished and been replaced by a mass of dark brown precipitate of manganese dioxide. When the liquid is cold, a stream of sulphur dioxide is passed in until the manganese dioxide is dissolved as manganese sulphate. The liquid is allowed to cool and the benzoic acid, which separates, is filtered at the pump, washed with a little cold water, and recrystallised from hot water; m.p. 121°. The yield is theoretical.

Benzoic acid is manufactured on a large scale from benzotrichloride by heating with milk of lime:

$$2C_6H_5.CCl_3+4CaO=(C_6H_5CO_2)_2Ca+3CaCl_2.$$

Calcium benzoate.

The lime salt is decomposed by acid, and the benzoic acid crystallises out. It forms colourless needles, which melt at 121°–122° and boil at 250°. Benzoic acid is volatile in steam, and its vapours affect the throat and nose, producing coughing and sneezing. It is soluble in hot, but sparingly so in cold water, and it dissolves in alcohol and ether. The insolubility of the majority of aromatic acids in water and their solubility in ether enable them to be separated and distinguished from many of the simpler aliphatic acids and hydroxy-acids. Benzoic acid forms well-defined salts. The calcium salt crystallises in long needles. Ferric benzoate is precipitated as a brown, amorphous powder from neutral solutions with ferric chloride. The acid is separated and precipitated from the salts on the addition of hydrochloric acid.

Aromatic Ketones

The aliphatic ketones contain two alkyl radicals linked by a ketone group. In the aromatic ketones one radical is aromatic, the other may be aliphatic or aromatic. **Acetophenone,** or phenyl methyl ketone, and **benzophenone,** or diphenyl ketone, are two typical examples of aromatic ketones :

$C_6H_5.CO.CH_3$. Acetophenone, or Phenyl methyl ketone.

$C_6H_5.CO.C_6H_5$. Benzophenone, or Diphenyl ketone.

The aromatic ketones are usually crystalline substances with a pleasant smell and in chemical characters resemble the aliphatic ketones. The methods of preparation will be illustrated in the case of acetophenone and benzophenone.

Acetophenone, Phenyl methyl ketone, $C_6H_5.CO.CH_3$, is obtained by distilling a mixture of calcium benzoate and acetate :

$$\begin{matrix}(C_6H_5.CO_2)_2Ca \\ (CH_3.CO.O)_2Ca\end{matrix} = \underset{\text{Acetophenone.}}{2C_6H_5.CO.CH_3.} + 2CaCO_3.$$

A more convenient method is that of Friedel and Crafts already referred to (p. 254), in which a mixture of benzene, acetyl chloride, and aluminium chloride are allowed to react :

$$C_6H_6 + ClCO.CH_3[+AlCl_3] = C_6H_5.CO.CH_3 + HCl.$$

When the reaction, which proceeds spontaneously, is complete, the product is shaken with caustic soda solution, and the undissolved oil removed and distilled.

Acetophenone is a colourless, crystalline compound with a fragrant smell. It melts at 20° and boils at 202°. It is sometimes used as a hypnotic, under the name of **hypnone.** On reduction it yields the secondary alcohol, phenylmethylcarbinol, $C_6H_5.CH(OH).CH_3$, and on oxidation, benzoic acid, the aliphatic side-chain being removed. Acetophenone forms an oxime and a phenylhydrazone, and possesses the general characters of an aliphatic ketone.

Benzophenone, Diphenyl ketone, $C_6H_5.CO.C_6H_5$, is obtained by distilling calcium benzoate, and by the action of benzoyl chloride, or carbonyl chloride, on benzene in presence of aluminium chloride:

$$C_6H_6+ClCO.C_6H_5[+AlCl_3]=C_6H_5.CO.C_6H_5+HCl.$$
$$2C_6H_6+COCl_2[+AlCl_3]=C_6H_5.CO.C_6H_5+2HCl.$$

It is a fragrant-smelling, crystalline substance, which melts at 48° and boils at 162°.

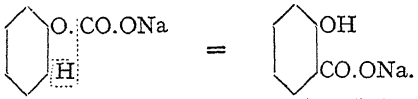
Salicylic acid, *o*-**Hydroxybenzoic acid,** $C_6H_4(OH).CO_2H$, is found as the methyl ester, $C_6H_4(OH).CO_2CH_3$, in oil of wintergreen, a fragrant liquid which is extracted from a heath (*Gaultheria procumbens*) grown in the United States and Canada. It is used for flavouring confectionery. It readily yields the acid on hydrolysis. A variety of synthetic methods exists for preparing salicylic acid, which a little reflection will suggest; but the manufacturing process, which is known as **Kolbe's reaction,** after its discoverer, is a peculiar one and unlike any previously described.

The process consists in heating to 120°–130° dry sodium phenate with carbon dioxide in closed vessels under pressure. It actually takes place in two steps. In the first reaction, sodium phenyl carbonate is formed:

$$C_6H_5ONa+CO_2=C_6H_5O.CO.ONa.$$
Sodium phenyl carbonate.

Then, at the high temperature of the reaction, an intramolecular change occurs, whereby the carboxyl group replaces

hydrogen of the nucleus in the ortho-position to the hydroxyl group:



Sodium phenyl carbonate. Sodium salicylate.

It is an interesting fact that if potassium phenate is heated to 220° in carbon dioxide, the product is exclusively the para-compound, or if potassium salicylate is heated to the same temperature, it is converted into *p*-hydroxybenzoic acid.

EXPT. 166.—**Preparation of Salicylic acid.**—This preparation should be commenced first thing in the morning. Dissolve 10 grams of caustic soda in about 10 c.c. of water in a small porcelain basin and add 23 grams of phenol. Heat the basin on wire-gauze over a very small flame, and, whilst holding it firmly with a small clamp (tongs are too insecure), keep constantly stirring with a glass rod. After a short time the mass becomes stiff and balls together. The basin should now be removed from the gauze, and the mass stirred and broken up as it cools. When still warm, it is sufficiently hard to powder in a mortar. It is quickly powdered and transferred to a small retort (200 c.c.) heated in an oil- or paraffin-bath to 130°–140°, and dried by passing over it a fairly rapid current of dry hydrogen from a Kipp. In about an hour all the moisture will be removed, and the body of the retort will appear dry. The light-coloured mass in the retort is allowed to cool whilst the hydrogen is passing through, then broken up and shaken into a mortar, when it is quickly powdered and replaced. The object of the above operation is to obtain perfectly dry, uncharred, and well-powdered sodium phenate, upon which the success of the preparation entirely depends. A moderate stream of carbon dioxide, dried through concentrated sulphuric acid, is now passed over the surface of the sodium phenate by means of a bent tube fixed through the tubulus of the retort, and terminating just above the substance. The temperature of the oil-bath is gradually raised from 140° to 180°–190°, whilst fresh surfaces are exposed by occasionally stirring with a glass rod inserted for a moment through the tubulus. At the end of four hours the temperature is raised to 190°–200° for another hour, and the process stopped. During the heating a considerable quantity of phenol distils, and solidifies in the neck of the retort, whilst the contents become dark coloured. The mass is shaken

out into a basin without disturbing the phenol in the neck, and the residue dissolved by filling the retort two-thirds full of water. This is poured into the basin containing the other portion, which soon dissolves. The solution is acidified with concentrated hydrochloric acid, which throws down impure salicylic acid in the form of a dark brown precipitate. When cold, the precipitate is filtered at the pump, and washed with a little cold water. A further quantity may be obtained by evaporating the filtrate to a small bulk. It is purified by dissolving in water, boiling with a little animal charcoal, and filtering. The filtrate deposits the acid, on cooling, in colourless needles which melt at 155°–156°, and give, when dissolved in water, a violet coloration with ferric chloride. The yield is about 6 grams.

On heating with soda-lime, salicylic acid loses carbon dioxide and is converted into phenol:

$$C_6H_4(OH).CO_2H = C_6H_5OH + CO_2.$$

EXPT. 167.—Grind up some salicylic acid, or its calcium salt, with double its bulk of soda-lime and heat over the flame. The smell of phenol is quickly detected.

Salicylic acid is a powerful antiseptic, and is frequently used as a substitute for phenol. **Salol,** the phenyl ester, and **betol,** the naphthyl ester, of salicylic acid, are also used as antiseptics. They are obtained by the action of salicylic acid on phenol, or naphthol (p. 305), in presence of an acid chloride (phosphorus oxychloride, or carbonyl chloride):

$$C_6H_4(OH)CO_2H + C_6H_5OH = C_6H_4(OH)CO_2C_6H_5 + H_2O.$$

Salicylic acid is also an antipyretic and the sodium salt is used in cases of rheumatism. The acetyl derivative, **aspirin,** has a similar effect, but is less of an irritant.

Gallic acid, 1:2:3:5-*Trihydroxybenzoic acid,* $C_6H_2(OH)_3CO_2H$, is one of six possible isomers. It is found associated with certain tannins (p. 300), from which it is separated by digestion with aqueous ether. The gallic acid dissolves in the ether, whereas the tannin substances are insoluble, but dissolve in the water present, and form a lower aqueous layer which can be separated. Gallic acid is also obtained by the hydrolysis of gallotannic, or digallic acid, which is the chief constituent of sumach

and of galls, the round excrescences formed on oak leaves and twigs by the puncture of the gall-fly.

Gallic acid crystallises in colourless needles, which lose carbon dioxide on heating, forming pyrogallol (p. 287). It gives a deep blue coloration or precipitate with ferric chloride, and when shaken with potassium cyanide, a pink solution which fades on standing, but reappears on again shaking. In alkaline solution it rapidly darkens in the air by oxidation. It does not precipitate gelatine, and can by this means be distinguished from the tannins.

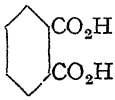
The Tannins is the name given to the active constituents of those substances which are used in tanning skins. The object of tanning is to prevent putrefactive changes, and to render the skin permanently flexible and porous. The hair is first removed from the skin, usually by the action of milk of lime, which at the same time causes the skin to swell. The lime is then dissolved out as far as possible by soaking the skins in fermenting dung, bran or old tan liquor, which contain organic acids (acetic, lactic, etc.) produced by fermentation. The skins are then steeped in tan liquor, which is the aqueous extract of a variety of vegetable substances, of which the following are among those commonly employed:

Oak bark.
Myrabolans (dried fruit of *Terminalia chebula*, India).
Valonia (acorn cup of *Quercus Ægilops*, Asia Minor).
Sumach (leaf of *Rhus coriaria*, Sicily).
Cutch (extract of wood of *Acacia catechu*, India).
Divi-divi (pod of *Caesalpina coriaria*, S. America).
Hemlock bark (*Abies canadensis*, N. America).

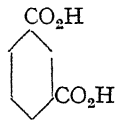
Although the tannins differ widely in chemical constitution and produce different effects on skins, they have the common property of precipitating gelatine from solution and forming insoluble compounds with it. It is this property which is effective in producing leather; for the process of tanning has been successfully imitated by the use of formaldehyde, or inorganic compounds such as chromic salts and alum, all of which render gelatine insoluble.

The Dibasic Acids

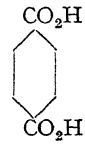
The most important dibasic acids are the three isomers, **phthalic, isophthalic,** and **terephthalic** acids, already mentioned as representing the final products of oxidation of the three isomeric xylenes (p. 259):



Phthalic acid.



Isophthalic acid.



Terephthalic acid.

The acids correspond to the aliphatic acids of the succinic acid series inasmuch as they form acid and neutral salts and esters.

Phthalic acid, Benzene-*o*-dicarboxylic acid, $C_6H_4(CO_2H)_2$, is made in large quantities for the preparation of fluorescein and the eosin dyes (p. 286), and for conversion into anthranilic acid, now extensively used in the manufacture of artificial indigo It is obtained by oxidising naphthalene with fuming sulphuric acid in presence of mercuric sulphate, which acts as a contact, or catalytic agent. The product is converted into phthalic anhydride by sublimation:

$$\underset{\text{Naphthalene.}}{C_{10}H_8}+9O=\underset{\text{Phthalic acid.}}{C_6H_4(CO_2H)_2}+2CO_2+H_2O.$$

$$C_6H_4(CO_2H)_2=C_6H_4\begin{matrix}CO\\ \diagup\ \diagdown\ O\\ CO\end{matrix}+H_2O.$$

Phthalic anhydride.

The conversion of naphthalene into phthalic anhydride is adduced as affording valuable evidence of the structure of naphthalene, by indicating the probable existence in naphthalene of a benzene nucleus (p. 304).

Expt. 168.—**Preparation of Phthalic acid.**—A mixture of 15 grams of naphthalene, 120 c.c. of concentrated sulphuric acid, and 7·5 grams of mercuric sulphate is placed in a retort (300 c.c.). The retort is clamped with the neck sloping upwards, and heated gently over wire-gauze with occasional shaking until the liquid

surface layer of naphthalene dissolves. The retort is now placed in the ordinary position, with the neck sloping down, to which a condenser tube is attached by means of a roll of asbestos paper, or a lute of plaster of Paris. The end of the condenser tube is provided with a receiver containing water (100 c.c.), and cooled in cold water.

The retort is now heated (at first cautiously and then strongly) over the bare flame, and the contents distilled. The liquid rapidly darkens in colour. At about 250° oxidation begins, with evolution of sulphur dioxide, which becomes very vigorous as the temperature of the liquid rises to the boiling-point. A little naphthalene first distils, and after a time crystals of phthalic anhydride appear in the condenser tube, whilst phthalic acid collects in the receiver. The distillation is continued until the residue becomes viscid or even dry. The contents of the receiver, when cold, are filtered and washed, and then dissolved in caustic soda. Any undissolved naphthalene is removed by filtration, and the acid reprecipitated by hydrochloric acid. The acid may be recrystallised from water or dilute alcohol. The yield is about 7 grams.

$$C_{10}H_8+9H_2SO_4=C_6H_4(CO_2H)_2+2CO_2+9SO_2+10H_2O.$$

Heat about 0·25 gram of the anhydride with 0·5 gram of resorcinol in a test-tube over a small flame for a few minutes, so that the temperature remains at about 200°. Cool, dissolve in dilute caustic soda solution, and pour into water. A green fluorescence is produced, due to the formation of fluorescein (p. 286).

QUESTIONS ON CHAPTER XXIII

1. Describe two methods of obtaining benzyl alcohol. How would you distinguish benzyl alcohol from the isomeric phenols ? Give the formulæ of the latter compounds.

2. Describe two methods by which benzaldehyde is prepared. Give details of the process, including the method of purification.

3. How would you prove by its properties and reactions that the chief constituent of bitter almond oil is an aldehyde ? In what respect do such aldehydes differ from acetic aldehyde ?

4. Describe the action of the following reagents on benzaldehyde : (1) caustic potash, (2) ammonia, (3) nitric acid.

5. Describe a method for preparing aromatic ketones, and give an example of their behaviour with reducing agents.

6. How may benzoic acid be prepared from each of the following substances: benzene, toluene, phenylcyanide, benzaldehyde, and benzyl alcohol? Which of these methods is of general application, and might be employed for the preparation of acetic acid?

7. Compare the physical and chemical properties of the aliphatic and aromatic acids by reference to acetic and benzoic acid.

8. Describe the preparation of benzoyl chloride and the action upon it of (1) ammonia, (2) aniline, (3) alcohol, (4) sodium benzoate. Give equations.

9. Describe a common method for obtaining benzoic esters.

10. Explain *Kolbe's reaction* by reference to the synthesis of salicylic acid. Mention any reactions by which salicylic acid may be identified and distinguished from the *p*- and *m*-hydroxybenzoic acids. How is salicylic acid converted into phenol?

11. Give an account of the *tannins* and their use in the preparation of leather. Name some tannin-containing products.

12. Describe the preparation of phthalic acid from naphthalene, isophthalic acid from *m*-xylene, and terephthalic acid from *p*-toluidine.

13. How is phthalic acid prepared? Describe its constitution and state how it may be transformed into benzoic acid and benzene.

CHAPTER XXIV

NAPHTHALENE AND ANTHRACENE

Naphthalene, $C_{10}H_8$, is contained in the middle oil distillate of coal-tar (p. 247), from which, on standing, a portion frequently crystallises. A further quantity is obtained by fractionating the same oil after the phenol has been separated with caustic soda (p. 280). When the uncrystallisable oil, which first distils, is removed, the subsequent distillate solidifies. This is impure naphthalene. It is purified by treatment with a little strong sulphuric acid, which forms soluble sulphonic acids with the impurities, so that on washing with water the latter are dissolved out. The naphthalene is then sublimed or distilled in steam. It crystallises in plates, which melt at 79° and boil at 218°.

Naphthalene is extremely volatile, even far below its boiling-point, so that in the coal-gas manufacture a little of it passes through the scrubbers and purifiers and finds its way into the gas-pipes, where it occasionally accumulates in sufficient quantity to obstruct the flow of gas. It burns with a luminous, smoky flame.

Naphthalene acts as a vermin killer and as a mild antiseptic; but its chief industrial use is in the manufacture of indigo and of certain azo-dyes.

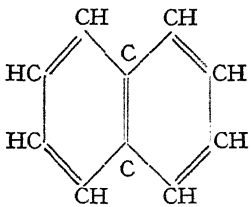
Naphthalene resembles benzene in its chemical properties. It can be chlorinated, brominated, nitrated, and sulphonated in the same way as benzene, and gives very similar products. The following are the formulæ of some of these products:

$C_{10}H_7Cl$.	$C_{10}H_7O_2N$.	$C_{10}H_7.SO_3H$.
Chloronaphthalene.	Nitronaphthalene.	Naphthalene sulphonic acid.
$C_{10}H_6Cl_2$.	$C_{10}H_6(NO_2)_2$.	$C_{10}H_6(SO_3H)_2$.
Dichloronaphthalene.	Dinitronaphthalene.	Naphthalene disulphonic acid.

Naphthalene forms amino-compounds (naphthylamines), which, like the amino-derivatives of benzene, can be diazotised. The sulphonic acids can be converted into phenols (naphthols) by fusion with caustic alkalis; or into cyanides (naphthyl cyanides) by distillation with potassium cyanide.

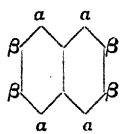
Structure of Naphthalene.—From the close analogy existing between naphthalene and benzene, one is naturally led to infer that naphthalene contains a benzene nucleus, and this view is apparently confirmed by the behaviour of naphthalene on oxidation; for it readily yields phthalic acid, as we have just seen.

The formula is usually represented as containing two benzene nuclei with two carbon atoms in common. It is therefore termed a hydrocarbon with **condensed nuclei.**



Formula for Naphthalene.

It therefore follows that of the 8 hydrogen atoms 4 will occupy a different position from the other 4 and these are known respectively as α and β positions.



Consequently, two mono-derivatives of naphthalene should exist in which the group occupies either an α or β position. This is found to be the case and two mono-derivatives of all the simpler compounds are known.

Anthracene, $C_{14}H_{10}$ (*ἄνθραξ*, coal), occurs with its isomer phenanthrene and a variety of other compounds in the last portion of the distillate from coal-tar, known as anthracene oil

(p. 247). The dark-coloured liquid deposits on standing a light-brown, crystalline mass consisting of impure anthracene. It is filtered in a filter press and washed with solvent naphtha free from adhering oil. The crystalline, pepper-coloured mass contains about 50 per cent. of anthracene, and is known commercially as **50 per cent. anthracene.** This forms the raw material which is used on an extensive scale in the manufacture of alizarin and allied colouring matters (p. 307). The crude anthracene may be purified by distillation with the addition of a little solid caustic potash.

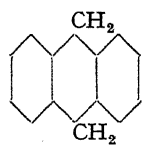
Pure anthracene crystallises from benzene and other solvents in colourless plates with a lustrous surface and blue fluorescence. It melts at 213° and boils at 351°, and forms a compound with picric acid which crystallises in red needles.

EXPT. 169.—Dissolve picric acid and anthracene in about equal molecular proportions in glacial acetic acid and pour them together. Red crystals soon deposit, and melt at 138°.

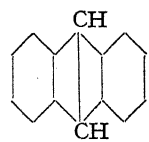
The majority of oxidising agents convert anthracene into anthraquinone:

$$\underset{\text{Anthracene.}}{C_{14}H_{10}} + 3O = \underset{\text{Anthraquinone.}}{C_{14}H_8O_2} + H_2O.$$

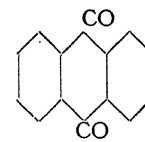
Seeing that anthracene is converted by reduction into anthracene hydride, and that anthracene is changed by oxidation into anthraquinone, the relation of the three is very simply expressed by the following formulæ:



Anthracene hydride



Anthracene.



Anthraquinone.

Alizarin, Dihydroxyanthraquinone, $C_{14}H_6O_2(OH)_2$, is the principal colouring matter of madder (*Rubia tinctoria*). Madder root has been used as a dyestuff in India and Egypt from the earliest times, and the process of dyeing cotton with a mordant is mentioned by Pliny. Madder owes its properties as a dye to alizarin and purpurin, which are present in the root as glucosides. The glucoside of alizarin is known as **ruberythric acid,** which is

hydrolysed by acids or ferments, and breaks up into glucose and alizarin:

$$\underset{\text{Ruberythric acid.}}{C_{26}H_{28}O_{14}} + 2H_2O = 2\underset{\text{Glucose.}}{C_6H_{12}O_6} + \underset{\text{Alizarin.}}{C_{14}H_8O_4}.$$

Madder root and the various extracts, which until fifty years ago were extensively employed in the production of **Turkey red** cloth and other dyed and printed fabrics, has been entirely superseded by artificial alizarin, purpurin, and similar colouring matters. The first important step in the synthesis of alizarin was made by Graebe and Liebermann in 1868, who found that when alizarin is heated with zinc dust it is converted into anthracene:

$$\underset{\text{Alizarin.}}{C_{14}H_8O_4} + Zn(OH)_2 + 5Zn = \underset{\text{Anthracene.}}{C_{14}H_{10}} + 6ZnO.$$

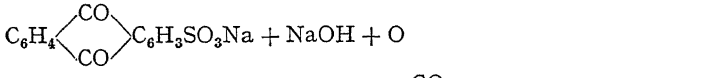
Anthracene, well known as a constituent of coal-tar, was recognised for the first time as the parent substance of alizarin. Now, alizarin contains two atoms of oxygen more than anthraquinone, which, from the solubility of alizarin in caustic soda, are probably present as hydroxyl groups. In order to introduce two hydroxyl groups into anthraquinone, Graebe and Liebermann converted it into dibromanthraquinone by bromination, and then fused the product with potash. They were fortunate in obtaining the one dihydroxy-derivative out of ten possible isomers, identical with alizarin:

$$\underset{\text{Dibromanthraquinone.}}{C_6H_4\langle{}^{CO}_{CO}\rangle C_6H_2Br_2} + 2KOH = \underset{\text{Alizarin.}}{C_6H_4\langle{}^{CO}_{CO}\rangle C_6H_2(OH)_2} + 2KBr.$$

Manufacture of Alizarin.—The somewhat costly process of Graebe and Liebermann was soon relinquished in favour of a method discovered simultaneously by these two chemists and by Perkin. The anthraquinone is heated with fuming sulphuric acid (containing 40 per cent. of sulphur trioxide) to 160°, and is converted into anthraquinone-β-monosulphonic acid. The sodium salt is then prepared by neutralisation of the sulphonic acid with sodium carbonate:

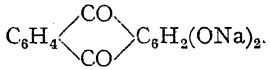
$$C_6H_4\langle{}^{CO}_{CO}\rangle C_6H_4 + H_2SO_4 = \underset{\text{Anthraquinone-}\beta\text{-sulphonic acid.}}{C_6H_4\langle{}^{CO}_{CO}\rangle C_6H_3.SO_3H} + H_2O.$$

The crystals of the sodium salt are fused in a closed vessel with caustic soda and a little potassium chlorate. The chlorate furnishes the necessary oxygen required by the reaction:



Alizarin.

The alizarin, present as the deep violet sodium compound, is extracted with water, in which it readily dissolves, and digested with milk of lime.



Sodium alizarate.

Insoluble calcium alizarate is thus formed, whilst the impurities remain in solution. The calcium alizarate is filtered and decomposed with hydrochloric acid, whereby the alizarin is precipitated in the form of a light brown, amorphous powder. It comes into commerce mixed with water in the form of a paste containing 10 or 20 per cent. of alizarin. In order to obtain alizarin in crystals, it may be sublimed or crystallised from cumene. It forms ruby-red prisms, which melt at 290° and sublime without decomposition.

Properties of Alizarin.—Alizarin is insoluble in water, but dissolves in the caustic alkalis with a violet colour, forming alizarates of sodium and potassium. Many of the metallic compounds are insoluble and are differently coloured. The aluminium alizarate is bright red, the ferric salt violet, and the chromic compound has a chocolate colour. A solution of sodium alizarate poured into a solution of one of the above metallic salts precipitates the insoluble alizarate, called a **lake**, and when washed and dried it is used as a pigment.

EXPT. 170.—Make moderately strong solutions of alum, ferric chloride, a mixture of alum and a few drops of ferric chloride and chromic chloride in separate cylinders, and pour into each a little

alizarin dissolved in a few c.c. of caustic soda solution. The metallic oxide precipitated by the alkali combines with the alizarin to form an insoluble lake (or metallic alizarate) which has a different colour in each case.

The formation of lakes explains the application of alizarin in the dyeing of cotton. Alizarin is insoluble in water, and has, moreover, no natural affinity for vegetable fibres. In order to attach it to cotton, the cloth or yarn is first impregnated with a salt, usually the acetate, of aluminium, iron, or chromium. It is then submitted to the action of heat, whereby the acetic acid is driven off and the metallic oxide left attached to the fibre. The cotton is said to be mordanted (p. 58). When steeped in water containing alizarin in suspension the oxide unites with the colouring matter and the cotton is permanently dyed. By using different mordants, or mixtures of them, a variety of tints is produced. In printing cotton cloth, the metallic salt is thickened with gum, or starch paste, and printed on the fabric, after which it is decomposed by passing over steam-heated iron plates. The cloth is then washed and dyed in alizarin, when the colour adheres to the pattern printed with the metallic salt.

EXPT. 171.—Cloth mordanted with stripes of different metallic oxides when moistened and left in a beaker of hot water containing a little alizarin in suspension takes up the dye and after a few minutes each stripe, according to the nature of the mordant, exhibits a different colour.

QUESTIONS ON CHAPTER XXIV

1. How are the separation and purification of naphthalene from coal-tar effected? Describe the manufacture of phthalic acid from naphthalene.

2. Compare naphthalene and benzene. Discuss the experimental evidence upon which the double-hexagon formula for naphthalene rests.

3. Give the number of mono- and di-derivatives of naphthalene. What is the system of nomenclature adopted to distinguish the isomers? Denote by figures the relative positions of the chlorine atoms in the ten dichloronaphthalenes.

4. Explain the commercial process for obtaining anthracene and anthraquinone.

5. Give an account of the properties of anthracene. What conclusions would you draw as to its structure from a consideration of the chemical properties of anthracene ?

6. Describe the production of alizarin. How is the dye applied to cotton ? What is the meaning of the terms *lake* and *mordant* ?

CHAPTER XXV

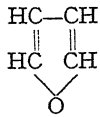
HETEROCYCLIC COMPOUNDS

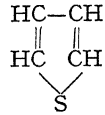
Heterocyclic Compounds.—The term heterocyclic is applied to ring compounds not composed wholly of carbon atoms, like those which have been described in preceding chapters (homocyclic compounds); but in which one or more of the links in the closed chain are supplied by other polyvalent elements, such as oxygen, sulphur, or nitrogen. We have already met with examples of this type of compound in the anhydrides of dibasic acids (p. 182), in which oxygen is an element in the ring; in uric acid (p. 229) and xanthine (p. 230) which form condensed, or double rings, consisting of a carbon and nitrogen skeleton. Such heterocyclic compounds are very common, and their synthesis forms an interesting chapter in recent research.

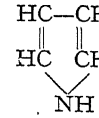
It would cover too much ground, and exceed the scope of the present volume, to give even a summary of all the different known classes of heterocyclic compounds. Some idea of their number and variety may be gathered from the examples which will be given. It should be pointed out that the most common kinds of ring compounds are those consisting of nuclei of 5 and 6 atoms, or condensed nuclei of the type of naphthalene and anthracene. Ring compounds composed of a larger or smaller number of atoms are less common.

We have selected for illustration three examples of heterocyclic compounds containing oxygen, sulphur, and nitrogen in a ring skeleton of 5 atoms. They are known as furfurane, thiophene,

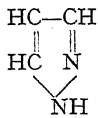
and **pyrrole**, and their structure is usually expressed by the following formulæ:

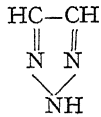

Furfurane.

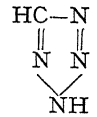

Thiophene.


Pyrrole.

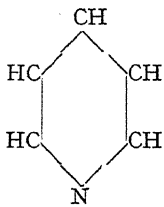
Pyrazole, Triazole, and **Tetrazole** represent 5-atom rings, containing 2, 3, and 4 nitrogen atoms:

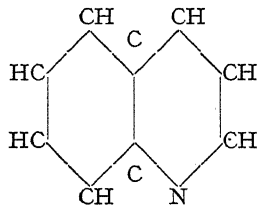

Pyrazole.

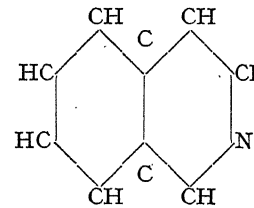

Triazole.


Tetrazole.

Examples of 6-atom rings are furnished by **pyridine, quinoline,** and **isoquinoline,** which may be compared with benzene and naphthalene, wherein an atom of nitrogen replaces one of the CH groups of the ring:


Pyridine.


Quinoline.


Isoquinoline.

These three substances may be regarded as the parent compounds of the **alkaloids,** which are described in the succeeding chapter.

All these substances have been obtained synthetically by methods which leave little doubt as to their structure.

Pyridine, C_5H_5N.—Pyridine is found in the light-oil distillate from coal-tar, from which it is separated by treatment with sulphuric acid in the ordinary course of purification. If an alkali is added to the acid liquid, a dark-coloured oil separates, containing pyridine and its homologues, together with quinoline, isoquinoline, aniline, etc., the constituents of which may be

partially separated by fractional distillation. Pyridine and its homologues, together with quinoline, are also present in considerable quantities in bone-oil, obtained by distilling bones.

Pyridine is a colourless liquid, which boils at 115° and mixes in all proportions with water. It has a strongly alkaline reaction towards litmus, and possesses a peculiar smell, which is characteristic of both pyridine and quinoline and many of their homologues. Pyridine is very indifferent to most reagents. It is unaffected by boiling strong nitric acid or chromic acid. Sulphuric acid only attacks it at a high temperature, forming a sulphonic acid. In the same way the halogens have little action on pyridine under conditions which in the case of benzene give rise to substitution products. With strong reducing agents, like strong hydriodic acid, nitrogen is eliminated in the form of ammonia, and the remainder of the molecule is reduced to pentane:

$$\underset{\text{Pyridine.}}{C_5H_5N} + 5H_2 = \underset{\text{Pentane.}}{C_5H_{12}} + NH_3.$$

Pyridine is a base, and forms salts with acids, which are usually soluble in water. It gives also a yellow, crystalline double salt with platinic chloride like other organic bases:

$$\underset{\text{Pyridine hydrochloride.}}{C_5H_5N.HCl} \qquad \underset{\text{Pyridine platinochloride.}}{(C_5H_5N.HCl)_2PtCl_4}.$$

It is, moreover, a tertiary base, for it neither combines with acetyl chloride to form an acetyl derivative, nor with nitrous acid to from a nitrosamine; but it unites with methyl iodide, and gives the quaternary ammonium compound, or pyridinium methyl iodide, $C_5H_5N.CH_3I$, which is a crystalline compound.

EXPT. 172.—Warm a mixture of equal volumes of pyridine and methyl iodide; a reaction sets in and the liquid boils. When cold, the crystalline quaternary compound is deposited.

Quinoline, C_9H_7N, was originally obtained by Gerhardt (1842) by distilling quinine, strychnine, and other alkaloids with caustic potash. The oil which distilled received the name of quinolein, which was changed to quinoline. Shortly afterwards (1846) Anderson isolated the same compound and many of its homologues from bone-oil. It is also present in coal-tar.

The most convenient source of quinoline is the synthetic method discovered by Skraup.

EXPT. 173.—**Preparation of Quinoline.**—A large round flask (1½—2 litres) is attached to a reflux condenser. A mixture of 24 grams of nitrobenzene, 38 grams of aniline, 120 grams of glycerol, and 55 c.c. of conc. sulphuric acid is poured in and heated on the sand-bath until the reaction sets in (ten to fifteen minutes), *i.e.* until white vapours rise from the liquid. The flask is now raised from the sand-bath or the burner extinguished, and when the first reaction is over the contents are gently boiled for two to three hours. The dark coloured product is diluted with water, and unchanged nitrobenzene driven over with steam. The residue is made strongly alkaline with caustic soda, and the oily layer (quinoline and aniline) distilled off with steam. In order to remove the aniline present, the distillate is acidified with sulphuric acid, and sodium nitrite added, until a sample of the liquid ceases to give the aniline reaction with sodium hypochlorite. It is then boiled, whereby the aniline is converted into phenol. The liquid is again made alkaline with caustic soda, and submitted to a third distillation with steam. The distillate is extracted with ether, dehydrated over solid caustic potash, and, after decanting and driving off the ether, the residue is distilled. The yield is 40 grams of a pale yellow oil.

$$\underset{\text{Aniline.}}{C_6H_5NH_2}+\underset{\text{Glycerol.}}{C_3H_5(OH)_3}+O=\underset{\text{Quinoline.}}{C_9H_7N}+4H_2O.$$

Quinoline is a colourless liquid with a smell resembling pyridine; but differs from pyridine in not being miscible with water, and it boils at a much higher temperature (236°). In chemical properties the two substances correspond closely. Quinoline is a tertiary base, and forms well-defined salts. The acid chromate, $(C_9H_7N)_2H_2CrO_4$, is sparingly soluble in water, and is precipitated in the form of yellow needles on the addition of potassium chromate to a solution of a salt of quinoline.

Isoquinoline, C_9H_7N, is isomeric with quinoline, and was first separated by Hoogewerff and van Dorp from the crude coal-tar quinoline by fractional crystallisation of the sparingly soluble sulphate. It is a colourless, crystalline substance, which melts at 21° and boils at 237°. It resembles quinoline in properties. Isoquinoline has increased in interest since its recognition as the parent substance of several alkaloids, such as **berberine,** the

alkaloid of barberry, and the alkaloids **narcotine, papaverine,** and **hydrastine,** which accompany morphine in opium.

QUESTIONS ON CHAPTER XXV

1. Explain the meaning of *heterocyclic compounds.* Give examples. Name some heterocyclic compounds composed of 5 atoms, and give their formulæ.

2. Give an account of the properties of pyridine.

3. Give an account of the chemical and physical properties of quinoline. Discuss its relation to pyridine. How is it prepared ?

4. What is isoquinoline, and where is it found ? What special interest attaches to it ?

CHAPTER XXVI

THE ALKALOIDS

The Alkaloids.—The medicinal properties, as well as the poisonous characters, of certain plants have long been recognised. Early in the nineteenth century Sertürner, a German apothecary, isolated the active principle of opium in the crystalline form and gave it the name of **morphium**. This discovery quickly led to others, and before long a large number of similar substances had been separated in the pure state from a variety of plants. They possessed basic properties, and were called **alkaloids** or **vegetable bases**; but whilst the name alkaloid is now applied to those compounds which have been shown to contain a pyridine, quinoline, or isoquinoline nucleus, the term vegetable base has a wider sense, and includes substances like caffeine, theobromine, betaine, etc. The alkaloids, then, are complex nitrogenous substances, possessing basic properties and a pyridine, or condensed pyridine nucleus. The structure of the majority of them is still unknown. Although the different individuals possess distinctive characters, they have many properties in common. They are optically active and usually lævo-rotatory in solution. They form insoluble compounds with many of the reagents which precipitate the proteins (p. 235), such as tannin, phosphomolybdic acid, and potassium mercuric iodide. They also give amorphous, brown precipitates with iodine solution. They have an alkaline reaction, possess for the most part a bitter taste, and many of them are extremely poisonous. A few of the alkaloids (**conine, nicotine**) are liquids, but the majority are crystalline solids, which are insoluble in water, but

dissolve in most of the organic solvents, such as ethyl and amyl alcohol, ether, chloroform, etc. The salts, especially the chloride and nitrate, are very soluble in water, and from the solution the insoluble base is precipitated by alkalis. The platinochlorides are yellow, crystalline, and sparingly soluble substances. Most of the alkaloids are tertiary bases and form additive compounds with the alkyl iodides. As a rule they are present in the plant combined with organic acids, such as malic, citric, and lactic acids, or an acid peculiar to the alkaloid with which it is associated. In cinchona bark, for example, the alkaloids are combined with quinic acid; in aconite with aconitic acid, etc. With the salts of the alkaloids are frequently associated proteins, tannins, resins, essential oils, and other vegetable products which have to be dealt with in the process of extraction.

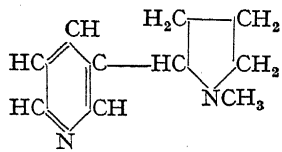
For each alkaloid a special process of extraction is employed, and for costly pharmaceutical preparations the estimation of the amount of alkaloid present in the raw material is effected by a recognised and carefully elaborated analytical method. A general scheme for extraction may be briefly indicated. The carefully ground material is digested with water, which dissolves the salt of the alkaloid, and the solution is then precipitated with an alkali or lime. If the alkaloid is volatile, like conine, it is separated by distillation in steam; otherwise it is either extracted with a volatile solvent such as ether, chloroform, amyl alcohol, etc., or filtered. The solvent in the first case is evaporated or shaken up with acid, which dissolves the alkaloid as the soluble salt; in the second case, the precipitate or its salt is recrystallised. It is seldom that a single alkaloid occurs in the plant; more frequently several are associated, and being chemically related, they are often difficult to separate.

The free alkaloids belong to different classes of compounds, such as amides or esters of organic acids in which the basic character predominates. The amides and esters are separable into a basic and acid constituent by hydrolysis. The basic portion often contains a hydroxyl, methoxyl, or carboxyl, or all three groups. **Piperine** is an amide, and breaks up on hydrolysis into the base piperidine and piperic acid; **atropine** is an ester,

and yields the base **tropine,** which is also an alcohol, and **tropic acid.** **Cocaine** represents a still more complex type, for the basic portion contains both a hydroxyl and carboxyl group.

Nicotine, $C_{10}H_{14}N_2$, is found in combination with malic and citric acids in tobacco leaves (in quantities varying from 0·6 to 8 per cent.), from which it is removed by distilling with milk of lime. The alkaloid passes into the distillate, which is extracted with ether. Nicotine is an oil which boils at 247°, and is lævo-rotatory. It is very soluble in water, has a strong and disagreeable smell, possesses a burning taste, and is a powerful poison. It is converted into nicotinic acid on oxidation with potassium permanganate or chromic acid.

It has recently been prepared synthetically, and both the dextro- and lævo-modifications are known. It is an interesting fact that the natural, lævo-rotatory alkaloid is much the stronger poison. The substance is represented by the following formula:



Atropine, $C_{17}H_{23}NO_3$, is a constituent of deadly nightshade (*Atropa belladonna*), henbane (*Hyoscyamus niger*), and thorn-apple (*Datura stramonium*), in which it is associated with **hyoscyamine, hyoscine,** and several other alkaloids. The extracted juice is mixed with caustic potash and shaken up with chloroform. The chloroform solution of the alkaloids is evaporated, and the residue extracted with dilute sulphuric acid, which dissolves the atropine as the sulphate, from which the base is precipitated by alkalis. Atropine crystallises in prisms, which melt at 115°. It is a strong base and forms well-defined salts. Atropine sulphate is used in ophthalmic cases for dilating the pupil of the eye. It is a strong poison.

EXPT. 174.—**Test for Atropine.**—Moisten a minute quantity of atropine with strong nitric acid, and evaporate it to dryness on the

water-bath. Add to the yellow residue a few drops of alcoholic potash. A violet solution is obtained.

Cocaine, $C_{17}H_{21}NO_4$.—The alkaloid is obtained from the leaves of *Erythroxylon coca,* in which several closely related alkaloids occur. The leaves are extracted with water and lead acetate is added to precipitate tannin and other substances; the filtered solution is then freed from lead by means of hydrogen sulphide; the filtered liquid is made alkaline, and the cocaine extracted with ether. Cocaine is a crystalline substance, which melts at 98°. The hydrochloride, $C_{17}H_{21}NO_4.HCl$, is soluble in water, and is used in medicine as a powerful local anæsthetic. Taken internally, it acts as a strong poison.

Cinchona Alkaloids.—The different varieties of cinchona bark which are grown in India, Ceylon, and South America are distinguished by the names of red, yellow, and pale bark, and contain a great number of alkaloids (amounting to 2 to 3 per cent. of the bark) united with quinic acid and a peculiar tannin, known as cinchotannic acid. The following are the most important members of the group—

$C_{20}H_{24}N_2O_2$.	$C_{19}H_{22}N_2O$.
Quinine.	Cinchonine.

The well-ground bark is mixed with milk of lime and evaporated to dryness. The mass is extracted with chloroform or petroleum, and the extract shaken with dilute sulphuric acid, which dissolves out the alkaloids as sulphates. The acid solution is neutralised with ammonia and concentrated. Quinine sulphate first separates, whilst cinchonine sulphate remains in the mother-liquors.

Quinine, $C_{20}H_{24}N_2O_2$.—When the sulphate of quinine obtained as described above is dissolved in water and alkali added, the free alkaloid is precipitated, and may be purified by crystallisation from alcohol. It forms glistening, white needles which, when anhydrous, melt at 177°. It has an alkaline reaction, a bitter taste, and is a feeble diacid base, forming a hydrochloride and sulphate of the following formulæ:

$C_{20}H_{24}N_2O_2.H_2SO_4+8H_2O$.	$C_{20}H_{24}N_2O_2.2HCl+2H_2O$.
Quinine sulphate.	Quinine hydrochloride.

Quinine sulphate is the salt commonly used in medicine. It has the property of lowering the temperature, and is a valuable remedy in cases of fever.

EXPT. 175.—**Tests for Quinine.**—Quinine is detected by the following tests. Use a solution of the hydrochloride prepared by adding a few drops of hydrochloric acid to the sulphate mixed with water. 1. Add to a little of the solution a few drops of iodine solution; a brown, amorphous precipitate is formed. This reaction is also given by other alkaloids (p. 316). 2. Add chlorine water and then ammonia in excess. An emerald-green colour is produced. 3. Add sodium carbonate solution and then a little ether. The free base is first precipitated, and then dissolves in the ether. Decant the ether on to a watch-glass and let it evaporate. Crystals of the base remain. 4. Dissolve a little quinine sulphate in a large volume of water, or add a few drops of glacial acetic acid and then a large volume of water. A blue, fluorescent liquid is obtained.

Cinchonine, $C_{19}H_{22}N_2O$, accompanies quinine in cinchona bark, and is especially abundant in the bark of *Cinchona huanoco*, which contains 2·5 per cent. It crystallises from alcohol in colourless prisms, and sublimes in a current of hydrogen in needles which melt at 250°. Its physiological action is similar to that of quinine, but less potent.

Opium Alkaloids.—The milky juice of the poppy capsule (*Papaver somniferum*), when dried, constitutes **opium,** and is a complex mixture of a very large number of alkaloids, resins, proteins, mineral salts, and organic acids. The alcoholic solution of opium is known as **laudanum.**

The following is an average analysis of opium, only the more important alkaloids being given:

	Per cent.		Per cent.
Morphine	10	Thebaine	0·3
Narcotine	6	Narceine	0·2
Papaverine	1	Meconic acid	4
Codeine	0·5	Lactic acid	1·25

In order to separate the alkaloids, the opium is extracted with hot water and boiled with milk of lime, which dissolves the bases, but precipitates the meconic acid. The liquid is filtered from the insoluble calcium meconate, and the filtrate boiled with

ammonium chloride until ammonia ceases to be evolved, whereby the lime is converted into calcium chloride and the morphine is precipitated together with other alkaloids.

Morphine, $C_{17}H_{19}NO_3+H_2O$, is a colourless crystalline compound, which melts at 230° and decomposes at the same time. It is very slightly soluble in water; is without smell; has a bitter taste, and is a strong narcotic. It has an alkaline reaction, and is a tertiary monacid base. The hydrochloride has the formula $C_{17}H_{19}NO_3.HCl+3H_2O$. Morphine may be distinguished from many of the alkaloids by its solubility in caustic alkalis. Its complete structure is not yet known. When distilled with zinc dust, it yields pyrrole, pyridine, quinoline, and phenanthrene.

EXPT. 176.—**Tests for Morphine.**—1. Add a few drops of ferric chloride to a solution of morphine chloride. A violet-blue colour is developed. 2. Add a little starch solution to a solution of morphine hydrochloride, and then a few crystals of iodic acid. Iodine is liberated by the morphine, and the starch turns blue. 3. Heat a little morphine with a few drops of strong sulphuric acid on the water-bath for half an hour. Cool the liquid, and add a drop of nitric acid. A violet colour is produced.

Strychnos Alkaloids.—The seeds of nux vomica (*Strychnos nux-vomica*) and St. Ignatius' beans (*Strychnos Ignatii*) contain the three alkaloids strychnine, brucine, and curarine, which are remarkable for their excessively poisonous character. At present little is known about their structure. On distillation with potash they yield quinoline.

To obtain the alkaloids from nux vomica, the seeds are powdered and extracted with alcohol. The extract is concentrated, and lead acetate added to precipitate tannin. The excess of lead is removed from the filtrate with hydrogen sulphide, and the alkaloids are then thrown down from the filtrate with ammonia. Brucine is separated from strychnine by its greater solubility in alcohol.

Strychnine, $C_{21}H_{22}N_2O_2$, crystallises in colourless prisms, which melt at 284°. It is nearly insoluble in water, but dissolves readily in acids. The hydrochloride has the formula $C_{21}H_{22}N_2O_2.HCl$, and the alkaloid is therefore a monacid base.

EXPT. 177.—**Test for Strychnine.**—A characteristic test for strychnine is the following :—Dissolve a crystal of strychnine in strong sulphuric acid, and add a little solid potassium dichromate, lead peroxide, or manganese dioxide. A violet colour is produced, which soon fades.

Brucine, $C_{23}H_{26}N_2O_4+4H_2O$, crystallises in colourless needles, which in the anhydrous state melt at 178°. It is a monacid base like strychnine, but is less poisonous.

EXPT. 178.—**Test for Brucine.**—Brucine is detected as follows :—Dissolve a little brucine in strong sulphuric acid, and add a crystal of potassium nitrate or a drop of nitric acid. A deep orange colour is developed, which changes to violet on the addition of a solution of stannous chloride. The presence of nitric acid is easily detected by this reaction.

EXPT. 179.—**The Molecular weight of Organic bases.**—The organic bases form, like ammonia, crystalline chloroplatinates with platinic chloride of the general formula $B_2H_2,PtCl_6$. By estimating the amount of platinum present in the salt, it is possible to calculate the molecular weight of the platinum compound, and consequently that of the base. Dissolve about 0·5 gram of an organic base (brucine, strychnine, quinine, etc.) in 10 c.c. of a mixture of equal volumes of concentrated hydrochloric acid and water. To the clear hot solution add excess of platinic chloride and let it cool. Yellow, microscopic crystals of the chloroplatinate of the base separate. (If the chloroplatinate of the base, such as aniline, is very soluble in water, it must be washed with strong hydrochloric acid, pressed on a porous plate and dried in a vacuum-desiccator over solid caustic potash.) Filter on the porcelain funnel with the pump and wash three or four times with small quantities of cold water. Press the precipitate down and dry on a porous-plate in the vacuum-desiccator. When thoroughly dry, weigh out about 0·5 to 1 gram of the compound into a porcelain or platinum crucible, and heat gently with the lid on, and then more strongly until the organic matter is completely burnt away. Cool the crucible in the desiccator and weigh.

The molecular weight of the salt is calculated from the weight w of the platinum, and W of the salt, according to the formula (the atomic weight of platinum being 195) :—

$$\frac{W \times 195}{w}.$$

To determine from this the weight of the base, it is necessary to deduct from the molecular weight of the salt that of H_2PtCl_6, and as two molecules of the base are contained in the salt, the result is halved.

Example—0·7010 gram of the chloroplatinate gave 0·2303 gram of platinum.

$$\frac{0{\cdot}7010 \times 195}{0{\cdot}2303} = 594{\cdot}2. \quad \text{M. W. of the salt.}$$

$$\frac{594{\cdot}2 - 409{\cdot}9}{2} = 92{\cdot}15.$$

Calculated for C_6H_7N: M. W.=93.

QUESTIONS ON CHAPTER XXVI

1. Name some of the characteristic features of the alkaloids. What is the origin of the name ?

2. Give either a general scheme or some special method for extracting the alkaloids from plants, and explain the object of the different steps.

3. How is nicotine prepared from tobacco ? Name some of its properties.

4. Name the plants in which atropine is found.

5. Describe a method for separating the cinchona alkaloids from bark. Compare the reactions of quinine and cinchonine.

6. Name some of the constituents of opium. What are the distinctive reactions for morphine ?

7. How would you distinguish strychnine from brucine ?

GENERAL QUESTIONS

1. What is the relation of urea to carbonic acid, of lactic to propionic acid, and of aniline to benzene? How is the first of each pair of substances prepared?

2. Give examples of the action of the following substances on organic compounds: phosphorus chloride, sulphuric acid, caustic soda.

3. What do you understand by the term optical activity? Explain its connection with the constitution of carbon compounds which manifest this property.

4. What is the chemical nature of the following substances: (*a*) fusel oil, (*b*) paraffin oil, (*c*) turpentine oil, (*d*) oil of bitter almonds, (*e*) vinegar, (*f*) methylated spirit, and (*g*) ether? How are these substances made, or from what sources are they obtained?

5. Give an account of the chemical character of (*a*) wood spirit, (*b*) petroleum, (*c*) butter, (*d*) cotton wool, and (*e*) nitroglycerin.

6. Write the structural formulæ for (*a*) any ester, (*b*) a dibasic organic acid, (*c*) a polyhydric alcohol, (*d*) an acid chloride, (*e*) an amide.

7. What is the action of phosphorus pentachloride on (*a*) ethyl alcohol, (*b*) acetic acid, and (*c*) acetaldehyde? What is the action of caustic potash on the products of these reactions?

8. What do you understand by a *double linkage*? Why do we assume its existence in acetaldehyde and in ethylene? What is the action of nascent hydrogen on these bodies?

9. What is the chemical nature of (*a*) chloroform, (*b*) vaseline, (*c*) formic acid, (*d*) formalin, (*e*) carbolic acid, (*f*) cream of tartar? How are these substances generally obtained?

10. What do you understand by the following terms: (*a*) paraffin, (*b*) acid chloride, (*c*) amide, (*d*) carbohydrate, (*e*) unsaturated compound? Give one example in each case with the structural formula.

11. Explain the chemical principles underlying the use of volatile combustible liquid as a fuel for motive power. What are the

chemical characteristics and principal sources of petrol, alcohol, and benzene?

12. Compare and contrast the properties of methane and acetylene and say how you would distinguish between them by experiments. Describe the difference in their behaviour when burnt and mention any special features connected with the use of acetylene as an illuminant.

13. Give the structural formulæ of the following substances, the methods of preparation and the principal properties of two of them: (*a*) formaldehyde, (*b*) chloroform, (*c*) urea, (*d*) ether, (*e*) acetyl chloride, and (*f*) phenol.

14. Explain what is meant by (*a*) a homologous series, (*b*) an unsaturated hydrocarbon, (*c*) an additive compound, (*d*) an ester.

15. Describe the preparation and properties of oxalic acid and cyanogen. What relation exists between these two substances? Give experimental evidence.

16. Name and give the structural formulæ of all substances represented by the following formulæ:

C_3H_8O C_3H_6O $C_3H_6O_2$ C_3H_9N

17. Define hydrolysis and give as many different examples of the process as you can.

18. Explain and illustrate the following terms: (*a*) acyl group, (*b*) condensation, (*c*) optical activity, (*d*) primary amine.

19. Describe the manufacture of the following: (*a*) soap, (*b*) ethyl alcohol, (*c*) acetic acid, (*d*) potassium cyanide, (*e*) ether.

20. Give your reasons for assuming that organic acids contain a carboxyl group and alcohols a hydroxyl group.

21. Explain and illustrate the terms: hydrolysis, reversible reaction.

22. Describe the preparation of pure specimens of (*a*) acetone from calcium acetate, (*b*) acetic acid from vinegar, (*c*) alcohol from cane-sugar, (*d*) chloroform from acetone, (*e*) acetaldehyde from ethyl alcohol.

23. How would you distinguish between a vegetable oil and a mineral oil (petroleum) and between stearin, stearic acid, paraffin wax, and soap?

24. Devise a method for separating the constituents of a mixture consisting of acetone, acetic acid, ethyl alcohol, and ethyl acetate.

25. Give the characteristic reactions for hydroxyl and aldehyde groups with examples and a list of reactions which the alkyl iodides undergo.

26. How would you ascertain the presence of (1) nitrogen, and (2) chlorine occurring in an organic compound? Describe how they may be estimated quantitatively.

27. In what respect does formic acid differ from palmitic and acetic acids? How is formic acid prepared?

28. What is meant by metamerism? How would you distinguish metameric compounds of the formulæ:

(1) $C_4H_{10}O$ (2) $C_4H_{11}N$ (3) $C_4H_8O_2$?

29. Devise a scheme for separating in a pure state the constituents of a mixture consisting of acetone, methyl alcohol, and acetic acid.

30. Describe in detail the preparation of ethyl ether, ethyl acetate, and acetic anhydride and compare their properties.

31. Describe briefly the manufacture of (1) spirits of wine, (2) soap, (3) vinegar. How could the organic acids be separated from the last two?

32. Discuss the isomerism and mode of preparation of the following: (1) the tartaric acids, (2) the lactic acids.

33. Describe the preparation and properties of the amino-acids. How can they be distinguished from amides, and what is their physiological significance?

34. Describe the most characteristic reactions which the following substances undergo: (1) glycerol, (2) ethylene, (3) malonic acid.

35. How have the following substances been synthesised: (1) urea, (2) succinic acid, (3) acetic acid?

36. Starting with acetic acid, how would you prepare the following: (*a*) methane, (*b*) ethane, (*c*) acetyl chloride, (*d*) acetamide, (*e*) acetic anhydride, (*f*) acetaldehyde?

37. Describe briefly the following manufacturing processes: (1) soap, (2) paraffin from shale, (3) spirits of wine, (4) acetic acid.

38. Explain the terms: (1) ureide, (2) glycol, (3) olefine, (4) sugar.

39. Describe in detail the preparation of pure alcohol from whisky and also of pure (1) ether, (2) ethyl acetate, (3) acetone, and (4) chloroform from commercial specimens. What tests would you apply to ascertain the purity of the substances in question?

40. Explain the meaning of the following terms employed in organic chemistry: *primary, polymeric, asymmetric, condensation, saponification, wax.* Give examples.

41. What compounds are obtained by the hydrolysis of the following substances:

(*a*) acetonitrile, (*b*) methyl isocyanate, (*c*) starch, (*d*) milk-sugar, (*e*) oxamide? Name the reagent you would employ in each case.

42. How would you distinguish between a *paraffin*, an *alcohol*, an *ester*, and an *amide*? Describe one method for preparing a member of each of these groups.

43. Describe a process for separating the constituents of a mixture containing ethyl acetate, ethyl alcohol, and formic acid.

44. Describe the action of the following reagents on alcohol, acetaldehyde, and acetic acid, separately: (*a*) caustic potash, (*b*) potassium dichromate and sulphuric acid; (*c*) strong sulphuric acid, (*d*) chlorine, (*e*) phosphorus pentachloride, (*f*) ammonia.

45. How would you prepare a pure specimen of (*a*) acetic acid from vinegar, (*b*) ethyl alcohol from beer, (*c*) fatty acids from soap, (*d*) acetone from acetic acid?

46. Discuss the general character of *unsaturated* compounds and illustrate your answer by reference to ethylene and acetylene. Do substances like acetaldehyde and methyl cyanide belong to the class of unsaturated compounds? Give your reasons.

47. How would you distinguish (1) acetyl chloride from acetic acid, (2) ethyl alcohol from acetone, (3) paraffin-wax from bees-wax, (4) butter from margarine?

48. Explain and illustrate the terms *homologous, metameric, polymerisation, condensation, substitution.*

49. How would you separate a mixture of formic acid, ethyl alcohol, and chloroform? What tests would you apply in order to identify them?

50. Illustrate the action of the various oxidising, reducing, and dehydrating agents used in organic chemistry. One example of each reagent will suffice.

51. Describe the separate action of chlorine, nitric acid, sulphuric acid, and nitrous acid upon (*a*) alcohol, (*b*) aniline.

52. Describe in outline the methods you would apply to determine the molecular weights of the following substances: (*a*) tartaric acid, (*b*) aniline, (*c*) benzene, (*d*) grape-sugar.

53. Explain by equations the following reactions:—

(*a*) Water on acetyl chloride.
(*b*) Hydrochloric acid on (i) ethyl alcohol, and (ii) ethyl isocyanide.
(*c*) Nitric acid on (i) glycerol and (ii) benzene.
(*d*) Caustic soda on potassium benzene sulphonate.
(*e*) Soda-lime on (i) salicylic acid, (ii) acetic acid.

54. Describe the general action of nitric acid and nitrous acid upon organic substances, and give examples.

55. Give examples to show the action on organic compounds of (*a*) phosphorus pentachloride, (*b*) nitric acid, (*c*) sulphuric acid.

56. Give one example of each of the different classes of organic compounds which form additive compounds and the general formulæ of the latter.

57. How would you propose to separate the following: (*a*) glycerol from fat, (*b*) uric acid from guano, (*c*) benzoic acid from gum benzoin, (*d*) benzene from coal-tar?

58. Each one of the following substances is separately dissolved in water: (*a*) cane-sugar, (*b*) sodium stearate, (*c*) aniline hydrochloride, (*d*) urea, (*e*) acetone. Describe any simple and effective method for identifying the different solutions.

59. Compare the general properties of a paraffin and an aromatic hydrocarbon. How would you distinguish between hexane and benzene?

60. How would you attempt to separate the following mixtures: (*a*) benzene and hexane, (*b*) phenol (carbolic acid) and ethyl alcohol, (*c*) acetic and benzoic acid, (*d*) urea and uric acid?

61. Discuss the structure of (*a*) glycerol, (*b*) toluene, (*c*) glucose.

62. Explain the terms: *Sandmeyer's reaction, side-chain, alkaloid, Friedel-Crafts' reaction.*

63. Discuss the term *acid* in its application to organic compounds. How can "carboxyl" be introduced into organic compounds, and what are its characteristic properties?

64. How would you distinguish (*a*) chlorotoluene from benzyl chloride, (*b*) acetone from propyl aldehyde, (*c*) cresol from benzyl alcohol?

65. Describe the preparation of the following: (*a*) Malonic acid from acetic acid, (*b*) urea from potassium cyanide, (*c*) formic acid from oxalic acid, (*d*) salicyclic acid from phenol.

66. How may the following groups be introduced into an organic compound and what are their characteristic properties (two or three in each case will suffice)?

(*a*) Hydroxyl, (*b*) nitro, (*c*) cyanogen, (*d*) amino, (*e*) ketone.

67. What are the characteristic products obtained by the destructive distillation (including the nature of the residue) of (*a*) wood, (*b*) coal, (*c*) bones, (*d*) bituminous shale? How are the products separated? State briefly for what industrial purpose they are used.

68. What is implied by the terms *nucleus* and *side-chain*? How can substitution of hydrogen by (*a*) chlorine, (*b*) hydroxyl, and (*c*) the amino-group be effected in the two positions, and what difference is there in the properties of each pair of substances formed?

69. How would you propose to separate a mixture consisting of aniline, acetone, benzene, and paraffin-wax so as to obtain each constituent in a pure state?

70. Illustrate by example the various uses of metals (in the metallic state) in organic synthesis.

71. For what purpose are the following reagents commonly employed: (*a*) acetyl chloride, (*b*) phenylhydrazine, (*c*) nitrous acid, (*d*) alcoholic potash, (*e*) phosphorus pentachloride? Give examples.

72. What is meant by the term "unsaturated compound"? Give examples. Does benzene belong to this class? State fully your reasons.

73. Discuss the action of (*a*) sulphuric acid, (*b*) nitric acid, and (*c*) the halogens on toluene.

74. Describe any general methods for the synthesis of aliphatic acids. What compounds have the formula $C_4H_8O_2$?

PROBLEMS

1. A compound of molecular formula C_2H_5NO when boiled with sodium hydroxide evolved ammonia and gave the sodium salt of an acid. The silver salt of this acid on analysis was found to contain 64·6 per cent. of silver. Discuss the structure of the original substance and its method of preparation.

2. A substance gave the following results on analysis :

0·197 gram gave 0·293 gram CO_2 and 0·150 gram H_2O ; by the Kjeldahl method 0·59 gram required 10 c.c. N/H_2SO_4 for neutralisation of the ammonia. The original substance when boiled with caustic soda evolved ammonia, and the dry residue when heated with soda-lime gave methane. What is the substance ? Explain the above reactions.

3. Calculate the molecular weight of a monobasic acid of which the ethyl ester gave the following results on hydrolysis :

1·5 gram of ester after boiling with 25 c.c. of a normal solution of alcoholic potash required 13·15 c.c. of normal sulphuric acid (coeff. = 1·14 for neutralisation).

4. The v.d. of an alcohol determined by V. Meyer's method gave the following numbers : 0·116 gram displaced 37 c.c. of moist air at 11° and 752 mm. (v.t. of water at 11°=9 mm.). What is the molecular formula of the alcohol and how would you determine its structure ?

5. A mono-acid organic base gave the following analytical results : 0·1 gram gave 0·2882 gram of CO_2 and 0·0756 gram H_2O. 0·2 gram gave 21·8 c.c. of N at 15° and 760 mm. 0·4 gram Pt. salt gave 0·125 gram Pt. (Pt.=195). Calculate the molecular formula of the base.

6. A liquid containing carbon, hydrogen, and oxygen had the following composition : C=68 per cent., H=13·6 per cent. On prolonged boiling with potassium dichromate and sulphuric acid and distilling the product, an acid distilled which was monobasic and gave a silver salt containing 51·7 per cent. of silver. Explain the nature of the acid and of the liquid from which it was prepared.

7. A liquid gave the following results on analysis : C=48·6, H=8·1, O=43·2 per cent. Vapour density 37. It was insoluble

in water but dissolved gradually on boiling with potash. What is the nature of the substance? How could you determine its constitution? How may it be prepared?

8. A compound of the formula C_7H_7NO loses ammonia when boiled with KOH, and from the resulting solution HCl precipitates a white, crystalline compound which, when dried and distilled with soda-lime, yields benzene. Discuss the nature of the above changes and explain how the original substance could be converted into aniline, phenol, and chlorobenzene.

9. Find the formula of three hydrocarbons from the following data:—

(*a*) 4 c.c. were exploded with 80 c.c. of air; 72 c.c. were left, and after absorption by potash 64 c.c. remained.

(*b*) 5 c.c. were exploded with 70 c.c. of air; 70 c.c. were left, and after absorption by potash 60 c.c. remained.

(*c*) 5 c.c. were exploded with 80 c.c. of air; 75 c.c. were left, and after absorption by potash 65 c.c. remained.

10. An organic compound has the following composition:

C=39·13; H=8·69; O=52·17

Boiling with acetyl chloride yielded an acetyl derivative which on hydrolysis with normal alcoholic potash and subsequent titration with acid gave the following result:

1·09 grams of acetyl compound neutralised 15 c.c. of normal alcoholic potash.

What is the probable nature of the substance?

Discuss its structure and its behaviour with different reagents.

11. A compound has the following percentage composition: C=81·55, H=4·8, N=13·6, and a vapour density of 51·15. It evolves ammonia on boiling with KOH, and on reduction with sodium and alcohol forms a base which reacts with nitrous acid, giving off nitrogen and yielding an alcohol. The alcohol can be oxidised to benzoic acid. What is the original substance? Explain the nature of the above changes.

12. A neutral crystalline organic compound contained the following amount of nitrogen: 0·178 gram gave 22·4 c.c. N. N.T.P. It was converted by nitrous acid with evolution of N into a liquid monobasic acid which gave the following result on analysis:

0·135 gram gave 0·198 gram CO_2 and 0·081 gram H_2O.

What are the above substances and what do you know about them?

13. Two isomeric substances have the following composition: C=78·5, H=8·4, N=13·0 per cent. In the analysis of the platinum salts 0·416 gram gave 0·130 gram of platinum (Pt=195). They dissolve in dilute HCl. On addition of $NaNO_2$ to the cold solutions, in the one case effervescence takes place, and in the other there is no apparent action till the solution is warmed, when effervescence also occurs. Explain the reason of this difference

in behaviour and how you would determine in other ways the nature of the compounds in question.

14. A dibasic acid containing 40·65 per cent. of carbon, 5·10 per cent. of hydrogen, and 54·25 per cent. of oxygen gave a silver salt containing 65 per cent. of silver. On heating this acid carbon dioxide was evolved and the resulting liquid was acid. The silver salt of the latter contained 59·6 per cent. of silver. What is the formula of the original substance and how would you propose to obtain it? What is the chemical change which takes place on heating it?

15. A substance which forms salts with both acids and bases has the following percentage composition :

$$C=61{\cdot}3\,;\ H=5{\cdot}1\,;\ N=10{\cdot}2\,;\ O=23{\cdot}3.$$

On heating it with lime it is transformed into a mono-acid base. The latter was converted into the chloroplatinate and on analysis 0·611 gram yielded 0·2 gram of platinum. What was the probable formula of the original substance, the mono-acid base and the platinum salt (Pt = 195)?

16. A neutral substance gave the following results on analysis : 0·2 gram gave 0·146 gram of CO_2 and 0·120 gram of H_2O ; 0·4 gram evolved ammonia (by Kjeldahl's method) which neutralised 13·3 c.c. of normal sulphuric acid. The substance in aqueous solution effervesced on the addition of sodium nitrite and HCl, and evolved ammonia on boiling with caustic soda solution. What is the probable formula of the original compound? To what class of substances does it belong? Give any general methods for their preparation. Explain the above two reactions.

17. Calculate the composition and give the molecular formula of a substance which on analysis gave the following data : 0·23 gram of the substance yielded 0·77 gram of CO_2 and 0·18 gram of H_2O. The vapour density was 46. Suggest the constitution of the substance. What experiments would you perform in order to decide the point?

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PRINTED IN GREAT BRITAIN BY R. CLAY AND SONS, LTD.,
BRUNSWICK STREET, STAMFORD STREET, S.E. I, AND BUNGAY, SUFFOLK.